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# Effect of partial damage efficiencies on the radiation-induced segregation in binary alloys

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## Abstract

A model of the radiation-induced segregation (RIS) in irradiated binary alloys, which takes into account the effect of the partial damage efficiencies is presented. Based on the model, the kinetics of RIS is investigated analytically and numerically. It is shown that no segregation exists when more intensive partial generation of point defects is compensated by corresponding greater diffusivity of the alloy component resulting in more intensive recombination on defect sinks. A simple criterion of the reversal of the RIS at the sample surface is obtained in terms of a critical temperature depending on the parameters related to the defect mobilities and partial damage efficiencies. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Decay of a supersaturated solid solution of point defects created in alloys by irradiation results in directed diffusion currents of defects from the bulk interior to grain and interphase boundaries. These currents can cause both the spatial segregation of the alloy atomic species [1,2] and a movement of the surfaces due to creation/destruction of new atomic layers resulting from defect annihilation at the surface.

According to the earlier analytical models [1,2], when mobilities of the alloy components via interstitials are equal, the current of vacancies to the free surface results in the depletion at the surface of an alloy component with larger diffusivity via vacancies. Hence, experimental evidence [3,4] of the existence of a temperature range, where accumulation of such an alloy component was observed at the grain boundary (reversal of RIS), was a surprise. Such qualitative discrepancy between theory and experiment is interesting not only from a funda-

mental point of view, but also for nuclear technology. This is because radiation-induced segregation (RIS) is expected to affect absorption/evaporation probabilities of point defects at a void surface and, hence, the kinetics of the radiation swelling [5].

Correlations between the value of the velocity of the sample surface and the reversal of RIS [3,4] were described recently [6] based on an approach which took into account the evaporation and absorption of point defects at a sample surface. An analytical criterion of the reversal of RIS was proposed there in terms of the critical velocity of the surface movement.

In this paper, we obtain another simple analytical criterion for the reversal of RIS, in terms of a critical temperature depending only on the microscopical characteristics of the defect diffusion as well as peculiarities of the damage production in an irradiated material.

## 2. Formulation of the problem

In this paper, we consider a two-component alloy as an ideal solid solution with random distribution of A- and B-atoms. These atoms can occupy both lattice sites and interstitial positions. Diffusion of the alloy atoms

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results from jumps of point defects (vacancies and interstitials) through the lattice. Trying to describe the reversal of RIS in the framework of the simplest analytical model, we do not take into account more complicated mechanisms of the defect migration or those whose validity for the atomic transport during irradiation is not finally established now (e.g. migration of small interstitial clusters [7] vs [8]). We describe here semi-infinite irradiated solid with a flat free surface and assume that dislocations and voids constitute the volume sinks for point defects. To take into account the defect accumulation in the irradiated alloy we introduce generation rates, both for vacancies and interstitials,  $G_v = G_i = G_A + G_B$  (where  $G_Y$  are the partial generation rates describing displacements of Y-atoms from lattice sites ( $Y = A, B$ )). For a given material these generation rates depend on particular damage efficiency of irradiation but for the presented model they are considered as input parameters and we suppose that the partial damage rates  $G_Y$  are given by the following equation:

$$G_Y = \frac{\eta_Y C_Y G_v}{\eta_A C_A + \eta_B C_B}, \quad (1)$$

where  $\eta_Y$  is the partial damage efficiency, and the effective generation rate  $G$  is taken in the following form:

$$G = \frac{G_v}{\eta_A C_A + \eta_B C_B}. \quad (2)$$

### 2.1. Governing equations of the model

The following system of equations describing temporal and spatial variations of the atomic and defect concentrations [6] can be assumed:

$$\frac{\partial C_v}{\partial t} = -\omega \nabla \vec{j}_v + G_v - R_A C_v C_{Ai} - R_B C_v C_{Bi} - k_v^2 D_v (C_v - \bar{C}_v^{eq}), \quad (3)$$

$$\frac{\partial C_Y}{\partial t} = -\omega \nabla \vec{j}_Y - G_Y + R_Y C_v C_{Yi} + k_{Yi}^2 D_{Yi} C_{Yi}, \quad (4)$$

$$\frac{\partial C_{Yi}}{\partial t} = -\omega \nabla \vec{j}_{Yi} + G_Y - R_Y C_v C_{Yi} - k_{Yi}^2 D_{Yi} C_{Yi}, \quad (5)$$

where  $\omega$  is the atomic volume,  $C_v$ ,  $C_Y$  and  $C_{Yi}$  the atomic concentrations of vacancies and Y-atoms occupying the substitutional and interstitial positions, respectively,  $R_Y$  the recombination factor for vacancies and Y-interstitials,  $k_\beta^2 = Z_\beta^d \rho_d$  ( $\beta = v, Ai, Bi$ ) and  $Z_\beta^d$  the bias factors for the absorption of  $\beta$ -defect by dislocations,  $D_\beta$  the diffusion coefficient of  $\beta$ -defects and  $\bar{C}_v^{eq}$  are the equilibrium vacancy concentrations at surfaces of the volume sinks averaged over the ensemble of volume sinks. We neglect the equilibrium interstitial concentrations at sink surfaces in system (3)–(5).

The diffusion currents in Eqs. (3)–(5) are defined by the following equations:

$$\omega \vec{j}_Y = -d_{Yv} C_v \nabla C_Y + d_{Yv} C_Y \nabla C_v, \quad (6)$$

$$\omega \vec{j}_{Yi} = -d_i \nabla C_{Yi}, \quad (7)$$

$$\omega \vec{j}_v = -D_v \nabla C_v + d_{Av} C_v \nabla C_A + d_{Bv} C_v \nabla C_B, \quad (8)$$

where  $D_v = d_{Av} C_A + d_{Bv} C_B$ ,  $d_{Y\beta} = (1/6) \lambda_\beta^2 z_\beta^2 v_{Y\beta}$  the partial diffusion coefficient [1],  $\lambda_\beta$  and  $z_\beta$  the diffusion jump length and the number of nearest neighbors for  $\beta$ -defect, respectively,  $v_{Y\beta} = v_{Y\beta}^0 \exp(-\Phi_{Y\beta}^m/T)$ ,  $v_{Y\beta}^0$  the attempt frequency of atomic jumps,  $\Phi_{Y\beta}^m$  is the Gibbs free energy of the Y-atom migration via the  $\beta$ -defect. In the presented paper, we do not investigate the effect of interstitials on RIS and equal partial diffusion coefficients of different alloy species via interstitials ( $D_{Yi} = d_{Yi} = d_i$ ) are assumed.

Substituting Eqs. (6)–(8) into (3)–(5) we obtain:

$$\frac{\partial C_v}{\partial t} = (d_{Av} C_A + d_{Bv} C_B) \nabla^2 C_v - (d_{Av} \nabla^2 C_A + d_{Bv} \nabla^2 C_B) C_v + G_v - R_A C_v C_{Ai} - R_B C_v C_{Bi} - k_v^2 D_v (C_v - \bar{C}_v^{eq}), \quad (9)$$

$$\frac{\partial C_Y}{\partial t} = d_{Yv} (C_v \nabla^2 C_Y - C_Y \nabla^2 C_v) - G_Y + R_Y C_v C_{Yi} + k_{Yi}^2 d_i C_{Yi}, \quad (10)$$

$$\frac{\partial C_{Yi}}{\partial t} = d_i \nabla^2 C_{Yi} + G_Y - R_Y C_v C_{Yi} - k_{Yi}^2 d_i C_{Yi}. \quad (11)$$

We assume equilibrium and space uniform initial conditions for the concentrations of defects and alloy species:

$$C_\beta(x, 0) = C_\beta^0, \quad (12)$$

$$C_Y(x, 0) = C_Y^0, \quad (13)$$

where  $x$  is the distance from the sample surface at the initial time and  $C_\beta^0$  are the initial equilibrium defect concentrations at the flat surface. We also demand that the values of all concentrations are bounded above and diffusion currents tend to zero in the bulk.

$$\vec{j}_Y|_{x \rightarrow \infty} = 0, \quad \vec{j}_\beta|_{x \rightarrow \infty} = 0. \quad (14)$$

When the evaporation and absorption of defects at the sample surface result in the surface movement, in addition to the boundary conditions for the diffusion currents of point defects at the sample surface

$$j_\beta|_{x=l(t)} = (j_\beta^O - j_\beta^P), \quad (15)$$

where  $j_\beta^O$ ,  $j_\beta^P$  are the number of  $\beta$ -defects evaporated and absorbed by a unit surface per second, respectively, we

have to write down an equation describing the surface movement:

$$\frac{dl}{dt} = \omega(j_{Ai} + j_{Bi} - j_v) |_{x=l(t)}, \quad (16)$$

where  $l(t)$  is the position of the sample surface at time  $t$ .

### 3. Analytical results

To obtain the criterion of the absence of RIS (or, that for the reversal of RIS), in this section we investigate modes when no segregation arises during the irradiation of the alloy.

Due to the flat surface of the sample, the characteristic lengths of our problem are the screening lengths for the diffusion of defects which are defined by the strengths of the volume sinks of the point defects [9]:

$$\lambda_{s\beta} = k_{\beta}^{-1}. \quad (17)$$

When surface movement results from the diffusion of point defects, it is easy to show that the characteristic times of defect diffusion to the surface,  $t_{\beta}^d$ , are much smaller than that of the surface movement  $t_l \sim \lambda_{s\beta}/|v|$  ( $v = dl/dt$  is the surface velocity) [6]:

$$(t_l/t_{\beta}^d) \geq C_{\beta}^{-1} \gg 1. \quad (18)$$

Moreover, the characteristic times  $t_Y^d$  of the component diffusion are also much larger than those of the defect diffusion [6]:

$$(t_Y^d/t_{\beta}^d) \sim C_{\beta}^{-1} \gg 1. \quad (19)$$

Taking into account Eqs. (18) and (19), below we shall use the coordinate system connected with the moving surface of the sample and assume that in the moving coordinate system spatial profiles of point defects are steady state and can be evaluated from the following equations:

$$D_v \nabla^2 C_v - (d_{Av} \nabla^2 C_A + d_{Bv} \nabla^2 C_B) C_v + \omega G_v - R_A C_v C_{Ai} - R_B C_v C_{Bi} - k_v^2 D_v (C_v - \bar{C}_v^{eq}) = 0, \quad (20)$$

$$d_i \nabla^2 C_{Yi} + \omega G_Y - R_Y C_v C_{Yi} - k_{Yi}^2 d_i C_{Yi} = 0, \quad Y = A, B. \quad (21)$$

We supply Eqs. (20) and (21) with the simplest initial and boundary conditions, assuming that the initial concentrations of point defects  $C_{\beta}^0$ , their equilibrium concentrations at sinks  $\bar{C}_{\beta}^{eq}$ , and those at a flat surface coincide:

$$C_{\beta x=l(t)} = \bar{C}_{\beta}^{eq} = C_{\beta}^0 = \exp\left(\frac{S_{\beta}^f}{k}\right) \exp\left(-\frac{H_{\beta}^f}{kT}\right), \quad (22)$$

where  $S_{\beta}^f$  and  $H_{\beta}^f$  are the defect formation entropy and enthalpy, respectively.

Neglecting the point defect recombination at the relevant temperatures [10,11], we obtain from Eqs. (20) and (21) the steady-state distribution of point defects when no segregation exists ( $\nabla C_Y = 0$ ):

$$C_v = C_v^0 + \frac{G_v}{D_v k_v^2} (1 - e^{-k_v x}), \quad (23)$$

$$C_{Yi} = \frac{G_Y}{d_i k_i^2} (1 - e^{-k_i x}). \quad (24)$$

Here and below we assume  $k_{Ai} = k_{Bi} = k_i$ .

In the same case ( $\nabla C_Y = 0, \partial C_v / \partial t = 0$ ) Eq. (10) for the component concentration can be also reduced to the following form:

$$-d_{Yv} C_Y \nabla^2 C_v - G_Y + k_i^2 d_i C_{Yi} = 0. \quad (25)$$

Substituting Eqs. (23) and (24) into Eq. (25), we obtain

$$d_{Yv} C_Y \frac{G_v}{D_v} e^{-k_v x} - G_Y e^{-k_i x} = 0. \quad (26)$$

We can see from Eqs. (25) and (26) that one of the modes, when no segregation exists in the irradiated alloy, arises at equal sink strengths ( $k_v = k_i$ ) when

$$\frac{d_{Av}}{d_{Bv}} = \frac{\eta_A}{\eta_B}. \quad (27)$$

Below we show that Eq. (27) gives also good approximation of the criterion of the segregation absence at arbitrary  $k_v \neq k_i$ .

It is clear from Eq. (27) that when no segregation exists, the more intensive partial generation of a certain type of interstitials has to be compensated by the correspondingly greater diffusivity of the correspondent component in order to allow more intensive recombination on sinks. Since the validity of this criterion depends on relations between the migration free enthalpies ( $\Phi_{Yv}^m$ ) and preexponential factors ( $v_{Yv}^0$ ) in the partial diffusivities, criterion (27) can be reformulated in terms of a critical temperature  $T_c$  (see Fig. 1):

$$T_c(k_v/k_i = 1) = \frac{\Phi_{Av}^m - \Phi_{Bv}^m}{\ln(\eta_B v_{Av}^0 / \eta_A v_{Bv}^0)}. \quad (28)$$

At a value of  $\eta_B/\eta_A = 1.1$  and for the material and environment parameters listed in Table 1 [4], we obtain that the critical temperature ( $T_c = 734$  K) falls in the temperature range where the reversal of RIS was observed in stainless steel [4].

It is useful to compare the applicability of criteria (27) and (28) and that based on the concept of the critical velocity of the sample surface [6]. Substituting Eqs. (7) and (8) into Eq. (16) one can obtain the surface

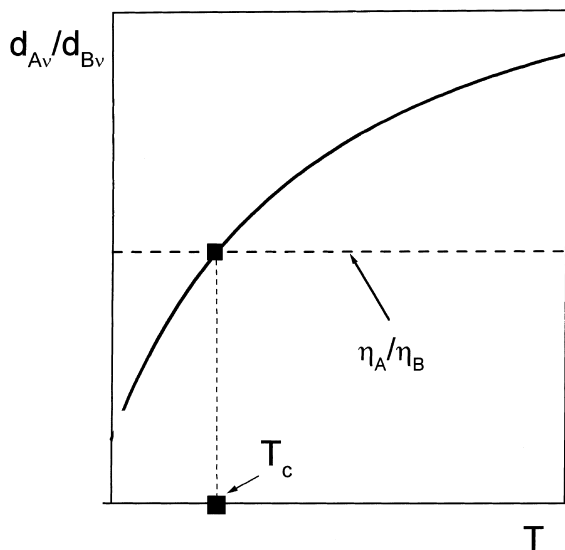


Fig. 1. Qualitative illustration of the criterium of RIS reversal. At the critical temperature  $T_c$  the difference of partial damage efficiencies is compensated by corresponding difference in mobilities of alloy components.

velocity resulting from the new layer formation/ destruction due to defect annihilation at the sample surface ( $\tilde{x} = x - vt$ ):

$$v - v_c = -[(d_{Av} - d_{Bv})C_v \nabla C_A]_{\tilde{x}=0}, \quad (29)$$

where the critical velocity  $v_c$  has the following form:

$$v_c = D_v \nabla C_v - d_i \nabla C_i|_{\tilde{x}=0}. \quad (30)$$

To derive Eqs. (29) and (30) we used the conservation law  $C_A + C_B + C_v = 1$  and assumed that  $d_{Bv}C_v \ll D_v = d_{Av}C_A + d_{Bv}C_B$  and  $C_i = C_{Ai} + C_{Bi}$ .

Table 1  
Main parameters used in the present calculation

Parameter	Notation	Value	
		Y = A	Y = B
Vacancy jump rate	$v_{Yv}^0$ (s <sup>-1</sup> )	$3.5 \times 10^{13}$	$1.5 \times 10^{13}$
Interstitial jump rate	$v_{Yi}^0$ (s <sup>-1</sup> )	$0.5 \times 10^{13}$	$0.5 \times 10^{13}$
Vacancy migration free enthalpy	$\Phi_{Yv}^m$ (eV)	1.2	1.14
Interstitial migration free enthalpy	$\Phi_{Yi}^m$ (eV)	0.9	0.9
Equilibrium interstitial concentration	$C_{Yi}^0$	0	0
Formation enthalpy of vacancy	$H_v^f$ (eV)	1.4	1.4
Formation entropy of vacancy	$S_v^f$	5k	5k
Dislocation density	$\rho_d$ (m <sup>-2</sup> )	$1 \times 10^{14}$	$1 \times 10^{14}$
Vacancy absorption bias factor	$Z_v$	1	1
Interstitial absorption bias factor	$Z_i$	1.2	1.2
Initial concentrations of the alloy species	$C_Y^0$	0.6	0.4
Damage rate	$G$ (dpa/s)	$(1-3) \times 10^{-4}$	$(1-3) \times 10^{-4}$
Damage efficiency	$\eta_Y$	1	1.1
Temperature	$T$ (K)	700–800	700–800

It is clear from Eq. (29) that the real velocity coincides with the critical one when either  $(d_{Av} - d_{Bv}) = 0$  or  $\nabla C_A = 0$ . At the equal damage efficiencies ( $\eta_B/\eta_A = 1$ ) both cases coincide resulting in the absence of RIS. When  $\eta_B/\eta_A \neq 1$  one of the alloy component can enrich the surface even when all defect diffusivities are equal. Then only the case  $\nabla C_A = 0$  really corresponds to the mode where no segregation is observed at the sample surface during irradiation, while the criterion based on the critical velocity can give ambiguous conclusions concerning the critical temperature (see Fig. 5).

Substituting Eqs. (23) and (24) into Eq. (30) we obtain the critical velocity corresponding to the spatially uniform distribution of alloy species ( $\nabla C_Y = 0$ ):

$$v_c = G(\eta_A C_A + \eta_B C_B) \left( \frac{1}{k_v} - \frac{1}{k_i} \right). \quad (31)$$

#### 4. Computer simulations

Below we apply computer simulations based on the general time depended form of the governing equations (9)–(11) for the verification of the obtained analytical results as well as for the more detailed investigation of RIS for the relevant parameters of irradiation and material.

##### 4.1. Features of the numerical algorithm used

The explicit finite difference scheme is applied to the numerical solution of equation set (9)–(11). To account for the boundary motion, the surface position is shifted by  $\delta l(t)$  after each time step according to relation (16). Defect currents to the surface are calculated from the solutions of Eqs. (9) and (11) for defect concentrations.

We assume that the values of  $\delta l(t)$  are positive when the surface material layers are removed by the defect currents and are negative in the opposite case. Creation or removal of the material layers at the sample surface is compensated by the following recalculation of the concentrations of alloys species at the boundary during the code execution:

$$C_Y(0, t + \tau) = \frac{C_Y(0, t) - \tau j_Y(0, t)}{(1 - \delta l(t))}, \quad (32)$$

where  $\tau$  is the time step value. In order to provide coordinate system movement with the boundary migration ( $x \rightarrow x - vt$ ), we also shift spacial grid by the value  $\delta l(t)$  at each time step. A linear interpolation is used to recalculate values of all concentrations in the nodes of the new grid:

$$C(x_m, t) \rightarrow C(x_m, t) + \frac{|\delta l|}{h} (C(x_{m+\text{sign}(\delta l)}, t) - C(x_m, t)),$$

$$m = 1 \dots (N - 1), \quad (33)$$

where  $m$  is an index of a node,  $h$  the spacial step ( $x_m = mh$ ), and  $N$  is the number of the node where the diffusion currents disappear:

$$C(x_N, t) = C(x_{N-1}, t). \quad (34)$$

The parameters used in the computer experiment are listed in Table 1 [4].

#### 4.2. Results and discussions

The numerical solution of the time depended general equations (9)–(16) proves the reversal of RIS at well

defined and unique temperature  $T_c(k_i/k_v)$  (e.g.  $T_c(1) = 734$  K for parameters listed in Table 1, see Fig. 2).

The kinetics of RIS are illustrated in Fig. 3. One can see from Fig. 3(a) that during the time  $t \approx 10^2$  s from the beginning of the irradiation the concentration profiles of the components become steady state in the coordinate system associated with the moving surface. Due to the

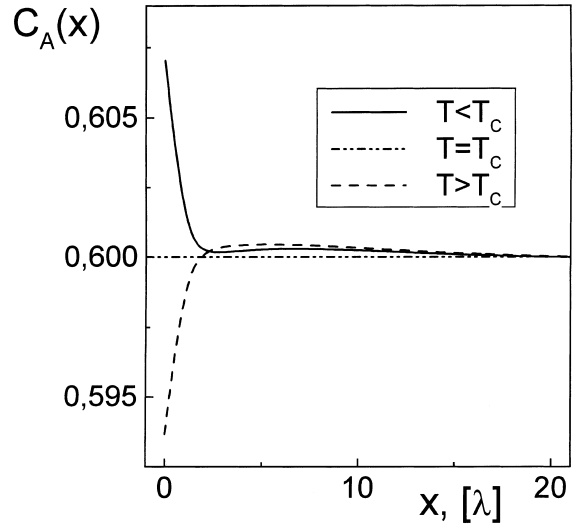
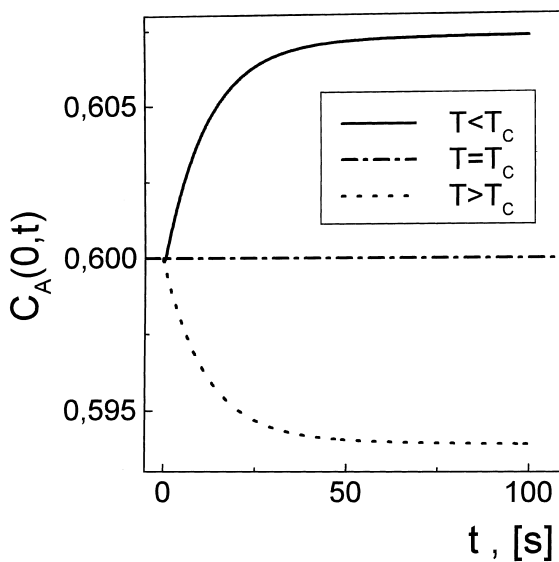
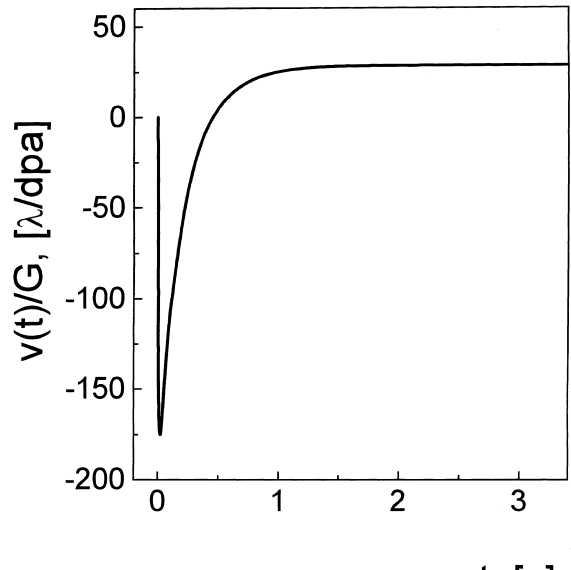


Fig. 2. The reversal of the steady-state concentration profiles of A-atoms  $C_A(x)$  at  $T < T_c$  and  $T > T_c$ . The distance from the surface to the sample interior is measured in units of the interatomic distance  $\lambda$ . The current position of the free surface is located in  $x = 0$ .



(a)



(b)

Fig. 3. The time evolution of: (a) the concentration of A-component at the surface; (b) the velocity of the free surface.

self-consistent description of the surface movement, the values of the concentrations of the alloy species at the surface  $C_Y(0, t)$  remain always bounded above during the irradiation.

The surface velocity tends to the steady-state value during the time which is much less than that for the concentration profiles of the alloy components (19) and comparable to that of the steady-state defect profile creation (see Figs. 3(a) and (b)). Transient negative values of the surface velocity can be ascribed to the noncompensated interstitial currents in the initial time due to the higher interstitial diffusivities.

The results of the numerical investigation of the influence of irradiation environment and material parameters on the critical temperature  $T_c(k_i/k_v)$  of the reversal of RIS are presented in Fig. 4. One can see that  $T_c(1)$  does not depend on the generation rate  $G$ , that confirms the analytical result (28) (curve 1). Since criterion (28) was obtained using the simplest suggestion  $k_i = k_v$ , in the same figure we present the results of the numerical simulations for  $k_i \neq k_v$ . In this case we obtain again the unique critical temperature for different generation rates as in the simplest analytical estimation (28). Moreover, variation of the critical temperatures at different  $k_i \neq k_v$  is negligible in comparison to values of these temperatures. Hence, one can apply the criterion (28) as a good approximation of the critical temperature of the reversion of RIS when  $k_i \neq k_v$ .

The results of the numerical investigation of the temperature dependence of the surface velocity are presented in Fig. 5. The surface velocity has broad flat maximum at the relevant temperatures where it practi-

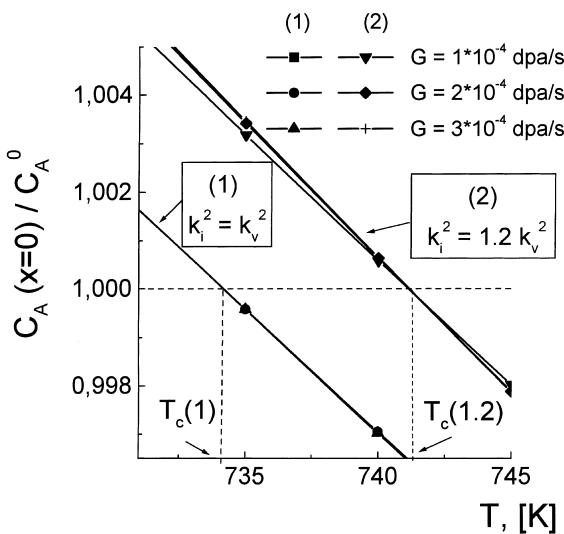


Fig. 4. Dependencies of the concentration of A-component at the free surface on bias factors, generation rate and temperature.

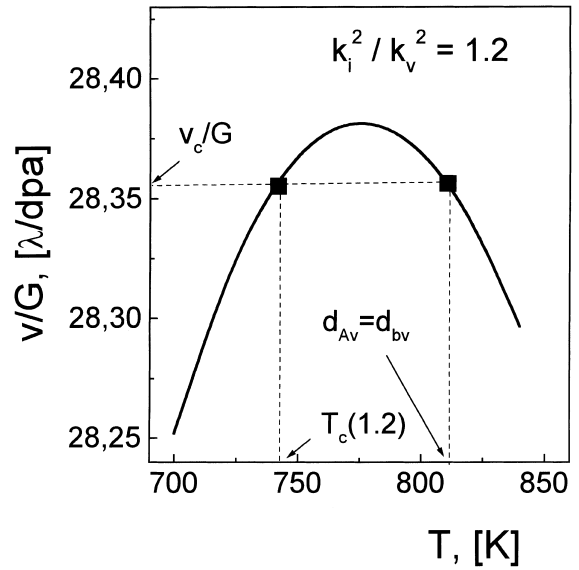


Fig. 5. Temperature dependence of the velocity of the free surface.

cally does not depend on the temperature and are defined mainly by the value of  $k_i/k_v$  ( $\Delta v/v_{max} \approx \Delta v/v_c \approx 1/150$ ). As was predicted analytically (see Eqs. (29) and (30)), non-monotonic temperature dependence of the surface velocity indeed results in two points of intersection with the line  $v = v_c$  when  $k_i \neq k_v$ . One of these points, at  $T_c(k_i/k_v)$ , really corresponds to the mode when no segregation exists in the irradiated alloy ( $\nabla C_Y = 0$ ).

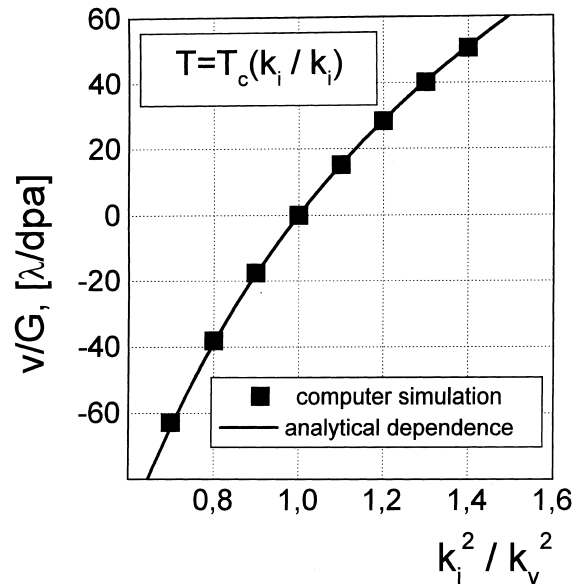


Fig. 6. Comparison between analytical and computer calculations of the critical velocity  $v_c/G$ .

Another one corresponds to the condition of equal diffusivities of the alloy components ( $d_{Av} = d_{Bv}$ ).

Additionally in Fig. 6 we compare the values of the critical velocity  $v_c$  obtained from the numerical solution of the general time depended governing equations (9)–(16), with their analytical approximations (31). A good agreement is achieved in the broad region of variation of the parameter  $k_i/k_v$ .

## 5. Conclusions

According to the results obtained, the reversal of RIS can be related to the balance between partial damage efficiencies and mobilities of alloy components.

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