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Effect of elastic stress field near grain boundaries on the radiation induced segregation in binary alloys

M.V. Sorokin, A.I. Ryazanov *

Russian Research Centre 'Kurchatov Institute', Kurchatov Sq., 123182 Moscow, Russia

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Abstract

An important problem of radiation resistance of structural materials for reactors (different types of steels, including steels doping by low radio-active elements) is their phase stability under neutron irradiation which is associated with the formation of solute radiation induced segregation (RIS) near grain boundaries. The diffusion of alloying elements under irradiation due to interstitial and vacancy diffusion mechanisms towards grain boundaries, which are perfect sinks for point defects results in the RIS formation near grain boundaries. Each grain boundary has the effective elastic stress field produced by the microstructure of grain boundaries. This elastic field can affect the formation of RIS in the dependence on an irradiation dose due to accumulation of impurity elements, gas atoms (helium), formation on grain boundary helium bubbles and precipitates especially at high doses of irradiation. The precipitates and overpressurised helium bubbles are the sources of internal stress fields too and they can dramatically change the effective stress field near grain boundaries. It will result in the redistribution of alloying elements near grain boundaries due to the additional diffusion driving force which is determined by the interaction energy of point defects with effective stress field near grain boundary.

1. Introduction

The formation of RIS near grain boundaries under neutron irradiation in reactor structural materials is one of the serious physical problems which affects the radiation resistance of these materials. Such physical phenomena as radiation embrittlement and intergranular fracture are caused by a redistribution of alloy components and segregation formation near grain boundaries. RIS and precipitate formation on grain boundaries can significantly change alloy composition and currents of point defects to defect clusters in matrix (voids, dislocation loop, precipitates) that can change the behavior of such very important phenomenon as radiation swelling in these materials. The investigations of RIS formation are based on analytical models taking into account inverse-Kirkendall effect [1–4]. Many papers [5–8] have been published concerning the description of this phenomenon under irradiation.

The width of distribution of RIS near grain boundary is located usually in the interval 10–100 nm. It is well known that the grain boundaries

* Corresponding author. Tel.: +7 495 196 91 77; fax: +7 495 196 05 31.
E-mail address: ryazanoff@comail.ru (A.I. Ryazanov).

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and interfaces can be modeled by discretely distributed array of grain boundary dislocation wall [9]. Each grain boundary dislocation interacts with point defects and impurity atoms due to produced elastic stress field near it. The interaction energy of grain boundary with point defects results in the additional driving force for point defects and impurity atoms in the currents of them to grain boundary. The characteristic distance where grain boundary (dislocation wall) can interact with point defects and can effect on diffusion processes is equal 3–20 nm [9]. So it is very interesting to investigate how the interaction energy of grain boundary with point defects and additional driving force can change the distribution of RIS near grain boundaries.

In this paper we investigate the effect of elastic stress fields near grain boundary on the formation of RIS in an irradiated binary alloy. For this aim we consider a two-component alloy as an ideal solution with random distribution of A- and B-types of atoms. These atoms can occupy both the lattice sites: substitution and interstitial positions. We will consider here a semi-infinite irradiated binary alloy with a flat surface and assume that dislocations and voids constitute the volume sinks for point defects in the matrix. Near the grain boundary we will take into account the effect of elastic stress field on point defect motion due to acting of an additional driving force on diffusion process which is determined by the interaction of point defects with the elastic stress field near grain boundary.

2. Governing equations of the model

The spatial profiles of the point defects near grain boundary are determined by the following steady-state system of diffusion equations for point defects:

$$-\omega\nabla\overrightarrow{j_{\mathrm{v}}}+G_{\mathrm{v}}-k_{\mathrm{v}}^2D_{\mathrm{v}}(C_{\mathrm{v}}-\overline{C}_{\mathrm{v}}^{\mathrm{eq}})=0 \tag{1}$$

$$-\omega\nabla\overrightarrow{j_{\mathrm{Yi}}}+G_{\mathrm{Y}}-(k_{\mathrm{Yi}})^2d_{\mathrm{i}}(C_{\mathrm{Yi}}-\overline{C}_{\mathrm{Yi}}^{\mathrm{eq}})=0;\quad \mathrm{Y}=\mathrm{A},\mathrm{B} \tag{2}$$

Here C_{v} and C_{Yi} are the atomic concentrations of vacancies and interstitials of Y-type, respectively; $\overrightarrow{j_{\mathrm{v}}}$ and $\overrightarrow{j_{\mathrm{Yi}}}$ are the point defects currents; ω is the atomic volume. D_β is the diffusion coefficient of the β-type of point defects ($\beta=\mathrm{v}$, Ai, Bi); $d_{\mathrm{Y}\beta}=(1/6)\lambda_\beta^2z_\beta\nu_{\mathrm{Y}\beta}$ is the partial diffusion coefficient [3]; λ_β, z_β are the diffusion jump length and the number of nearest neighbors for β-type of point defect, respectively; $\nu_{\mathrm{Y}\beta}=\nu_{\mathrm{Y}\beta}^0\exp(-\Phi_{\mathrm{Y}\beta}^m/T)$, $\nu_{\mathrm{Y}\beta}^0$ is the attempt frequency of atomic jumps; $\Phi_{\mathrm{Y}\beta}^m$ is the Gibbs free enthalpy of the Y-atom migration via the β-type of point defect.

$$D_{\mathrm{v}}=d_{\mathrm{Av}}C_{\mathrm{A}}+d_{\mathrm{Bv}}C_{\mathrm{B}} \tag{3}$$

Here C_{Y} ($\mathrm{Y}=\mathrm{A},\mathrm{B}$) is the atomic concentration of Y-atoms occupying the substitutional positions.

For simplicity the equal partial diffusion coefficients of the different alloy species via interstitials ($D_{\mathrm{Yi}}=d_{\mathrm{Yi}}=d_{\mathrm{i}}$) are suggested below. $\overline{C}_\beta^{\mathrm{eq}}$ is the equilibrium defect concentration at the surfaces of volume sinks averaged over the ensemble of the volume sinks.

The sink strengths in the bulk are given by:

$$k_\beta^2=Z_\beta^d\rho_{\mathrm{d}}+2\pi N_{\mathrm{V}}\left\langle Z_\beta^VR_{\mathrm{V}}\right\rangle,\quad x\geqslant\Lambda \tag{4}$$

Here Z_β^d are the bias factors for the absorption of β-type of point defect at the dislocations; N_{V}, R_{V}, and Z_β^{V} are the void volume density, radius and bias factor, respectively; $\langle\rangle$ denotes the average over the ensemble of the volume sinks; ρ_{d} is the dislocation density. Λ is the width of defect-free zone near the surface or the grain boundary [10–12], $k_\beta^2=0$ for $x<\Lambda$. In the following numerical calculations we will use $\Lambda=100\lambda$, where λ is the lattice spacing.

Defect accumulations during irradiation are described by generation rates, both for vacancies and interstitials, $G_{\mathrm{v}}=G_{\mathrm{i}}=G_{\mathrm{A}}+G_{\mathrm{B}}$ (where G_{Y} are the partial generation rates describing displacements of Y-atoms from lattice sites). These generation rates are considered as input parameters. We suppose that the partial damage rates G_{Y} are given by the following relations [7]:

$$G_{\mathrm{Y}}=\frac{\eta_{\mathrm{Y}}C_{\mathrm{Y}}G_{\mathrm{v}}}{\eta_{\mathrm{A}}C_{\mathrm{A}}+\eta_{\mathrm{B}}C_{\mathrm{B}}}=\eta_{\mathrm{Y}}C_{\mathrm{Y}}G, \tag{5}$$

where η_{Y} is the partial damage efficiency, and the effective generation rate G is defined as:

$$G=\frac{G_{\mathrm{v}}}{\eta_{\mathrm{A}}C_{\mathrm{A}}+\eta_{\mathrm{B}}C_{\mathrm{B}}} \tag{6}$$

At the surface or grain boundary ($x=0$) we suppose the equilibrium concentrations of point defects adjusted on elastic field energy:

$$\begin{aligned}C_\beta(0)&=\overline{C}_\beta^{\mathrm{eq}}\exp\left(-\tfrac{U_\beta}{T}\right)\\ \overline{C}_\beta^{\mathrm{eq}}&=\exp\left(\tfrac{S_\beta^{\mathrm{f}}}{k}\right)\exp\left(-\tfrac{H_\beta^{\mathrm{f}}}{kT}\right)\end{aligned} \tag{7}$$

Here S_β^{f} and H_β^{f} are the defect formation entropy and enthalpy, respectively, U_β is the interaction energy of point defects with the grain boundary.

We also demand that values of all concentrations are positive and finite, and all diffusion currents tend to zero in the bulk, far from the grain boundary.

$$\overrightarrow{j_\beta}|_{x\to\infty} = 0 \tag{8}$$

It should be noted that disbalance of vacancy and interstitial currents to a grain boundary results in the movement of the boundary [7,8]. But in this case it is possible to use coordinate system related with the moving boundary, keeping the form of Eqs. (1)–(2) and boundary condition (7).

2.1. Elastic stress field and point defect currents

The interaction energy of point defects with the grain boundary is determined by the elastic stress field near grain boundary (σ_{ij}), and it can be written in the following form

$$U_\beta = -\sigma_{ij}\varepsilon_{ij}^\beta \tag{9}$$

Here ε_{ij}^β is the strain distribution of β-type point defects. For the spherical symmetry of point defect (dilatation center) this value is given by the following relation:

$$\varepsilon_{ij}^\beta = \varepsilon_\beta \delta_{ij}$$

Here ε_β is the spherical dilatation of β-type point defects, δ_{ij} is the Kronecker symbol.

The model of a grain boundary as dislocation wall with an effective dislocation density is demonstrated in Fig. 1. Finally, the interaction energy of grain boundary with point defect can be written in the following form:

$$U_\beta = -Sp\widehat{\sigma}\varepsilon_\beta$$
$$Sp\widehat{\sigma} = \sigma_{xx} + \sigma_{yy}$$

Taking stress tensor components of elastic stress field near a dislocation wall in (x,y) coordinate system from [9] we obtain:

$$U_\beta = T\frac{\pi L_\beta}{h}\frac{\sin(2\pi Y)}{\mathrm{ch}(2\pi X) - \cos(2\pi Y)} \quad X = \frac{x}{h}, \quad Y = \frac{y}{h},$$
$$L_\beta = \frac{\mu b \varepsilon_\beta}{\pi(1-\nu)T} \tag{10}$$

Here μ is the shear module, T is the temperature, h is the average distance between dislocations on the grain boundary, b is the Burger's vector.

In the case of a strong interaction of point defects with a grain boundary ($L_\beta \gg h$) and for one dimensional diffusivity of point defects near it we can neglect the diffusion processes along Y-axes and further approximate in our calculations the interaction energy as

$$U_\beta \approx -TL_\beta\frac{2\pi}{h}\exp\left(-\frac{2\pi x}{h}\right) \tag{11}$$

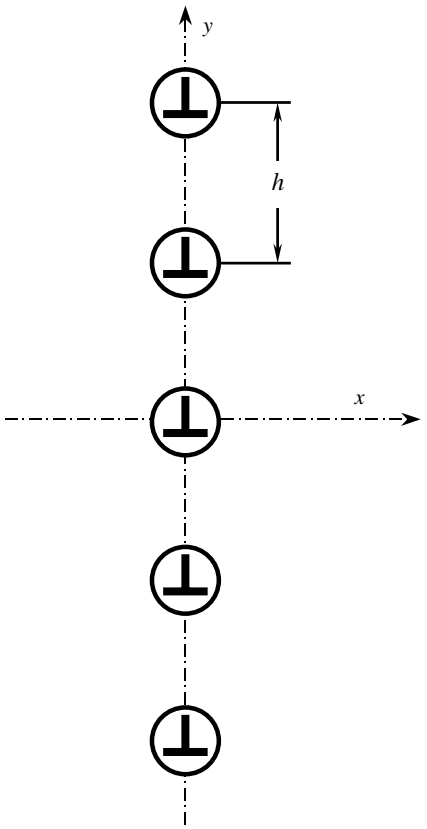

Fig. 1. Model of a grain boundary as a dislocation wall with the effective dislocation density.

The elastic stress field changes the potential energy barrier for diffusion jumps of point defects, and the point defects currents can be written by the following relations:

$$j_{\mathrm{Yi}}(x) = \frac{d_{\mathrm{Yi}}}{\lambda}\left(C_{\mathrm{Yi}}(x)\mathrm{e}^{-\frac{U_{\mathrm{Yi}}(x+\lambda)-U_{\mathrm{Yi}}(x)}{2T}} - C_{\mathrm{Yi}}(x+\lambda)\mathrm{e}^{-\frac{U_{\mathrm{Yi}}(x)-U_{\mathrm{Yi}}(x+\lambda)}{2T}}\right) \tag{12}$$

$$j_{\mathrm{Yv}}(x) = \frac{d_{\mathrm{Yv}}}{\lambda}\left(C_{\mathrm{v}}(x)C_{\mathrm{Y}}(x+\lambda)\mathrm{e}^{-\frac{U_{\mathrm{Yv}}(x+\lambda)-U_{\mathrm{Yv}}(x)}{2T}} - C_{\mathrm{v}}(x+\lambda)C_{\mathrm{Y}}(x)\mathrm{e}^{-\frac{U_{\mathrm{Yv}}(x)-U_{\mathrm{Yv}}(x+\lambda)}{2T}}\right) \tag{13}$$

Therefore, the currents of point defects are given by the relations with the drift terms proportional to the gradient of interaction energy:

$$\omega\overrightarrow{j_{Yi}} = -d_{Yi}\nabla C_{Yi} - d_{Yi}C_{Yi}\frac{\nabla U_{Yi}}{T} \quad (14)$$

$$\omega\overrightarrow{j_{Yv}} = d_{Yv}(C_v\nabla C_Y - C_Y\nabla C_v) - d_{Yv}C_YC_v\frac{\nabla U_v}{T} \quad (15)$$

Here $\overrightarrow{j_{Yv}}$ are the vacancy currents via Y-atoms. The total vacancy current is given:

$$\overrightarrow{j_v} = \overrightarrow{j_{Av}} + \overrightarrow{j_{Bv}} \quad (16)$$

Current of Y-atoms in the bulk has the opposite direction of the corresponding vacancy current:

$$\overrightarrow{j_Y} = -\overrightarrow{j_{Yv}} \quad (17)$$

Meanwhile, at the grain boundary we have the following boundary condition:

$$\overrightarrow{j_Y}|_{x=0} = (\overrightarrow{j_{Yi}} - \overrightarrow{j_{Yv}})_{x=0} \quad (18)$$

3. Numerical calculations

Generally, we should solve the system of equations for the diffusion profiles of atoms simultaneously with those for point defects. However, for the investigation of the elastic stress field effect, we are forced to take a spacial grid step smaller than the distance between edge dislocations in the grain boundary h, so such calculations would be too elaborate. Instead, we will analyze the special case, namely the condition for segregation reversal when $\nabla C_Y = 0$. Then:

$$\omega\overrightarrow{j_{Yv}} = -d_{Yv}C_Y\nabla C_v - d_{Yv}C_YC_v\frac{\nabla U_v}{T} \quad (19)$$

$$\omega\overrightarrow{j_v} = -D_v\nabla C_v - D_vC_v\frac{\nabla U_v}{T} \quad (20)$$

Substituting (20) and (14) into (1–2) we obtain the non-linear differential equations, which should be solved numerically.

$$\nabla^2 C_v + \nabla C_v\frac{\nabla U_v}{T} + C_v\frac{\nabla^2 U_v}{T} + \frac{G_v}{D_v} - k_v^2(C_v - \overline{C}_v^{eq}) = 0 \quad (21)$$

$$\nabla^2 C_{Yi} + \nabla C_{Yi}\frac{\nabla U_i}{T} + C_{Yi}\frac{\nabla^2 U_i}{T} + \frac{G_Y}{d_i} - (k_{Yi})^2(C_{Yi} - \overline{C}_{Yi}^{eq}) = 0 \quad (22)$$

Boundary conditions (7) and (8) are implied. Besides, we have to check whether the segregation has ceased:

$$\left.\frac{j_A}{j_B}\right|_{x=0} = \frac{C_A^0}{C_B^0} \quad (23)$$

The temperature at which the segregation ceased is called as the critical temperature – T_c, and without the elastic field could be calculated analytically [7,8]. The investigation of influence of the stress field is the main subject of the present computer calculations.

The explicit finite difference scheme was applied for the numerical solution of the system of Eqs. (21–22). It is convenient to utilize the lattice parameter λ as difference value. The search of critical temperature was carried out by the iterations. After solving of Eqs. ((21)–(22)) at the temperature T, we substituted (12) and (13) into (18) in order to check whether the relation (23) is satisfied or we have to change the temperature.

This equations in turn are solved by the method of successive approximations of $C_\beta(\lambda)$. This value is searched such that the diffusion currents disappear in the bulk according to (8) i.e.,

Table 1
The elastic field parameters

Parameter	Notation	Value	
		$\beta = v$	$\beta = i$
Field amplitude	L_β, λ	− 15	50
Distance between edge dislocations	h, λ	50	

Table 2
Main parameters used in the present calculations

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

$$C_\beta(\lambda N) = C_\beta(\lambda(N-1)) \tag{24}$$

where N is the node number of most remote from the surface ($x = 0$) node, selected so that $\lambda N \gg \max(h, \frac{1}{k_\beta})$.

The parameters used in the computer calculations are presented in Tables 1 and 2. Defect profiles, obtained by the numerical algorithm described above, when segregation is ceased ($\nabla C_Y = 0$) and consequently $T = T_c$, are shown at Fig. 2 for different values of L_β. When the elastic field is increased, the drift part of the point defect currents (the second term in r.h.s. of (14) and (20)) becomes much larger than for diffusion alone. So at large values of L_v, the alloy component current ratio on the l.h.s. of (23) tends to d_{Av}/d_{Bv}, and $T_c \to T_c(\eta_A/$

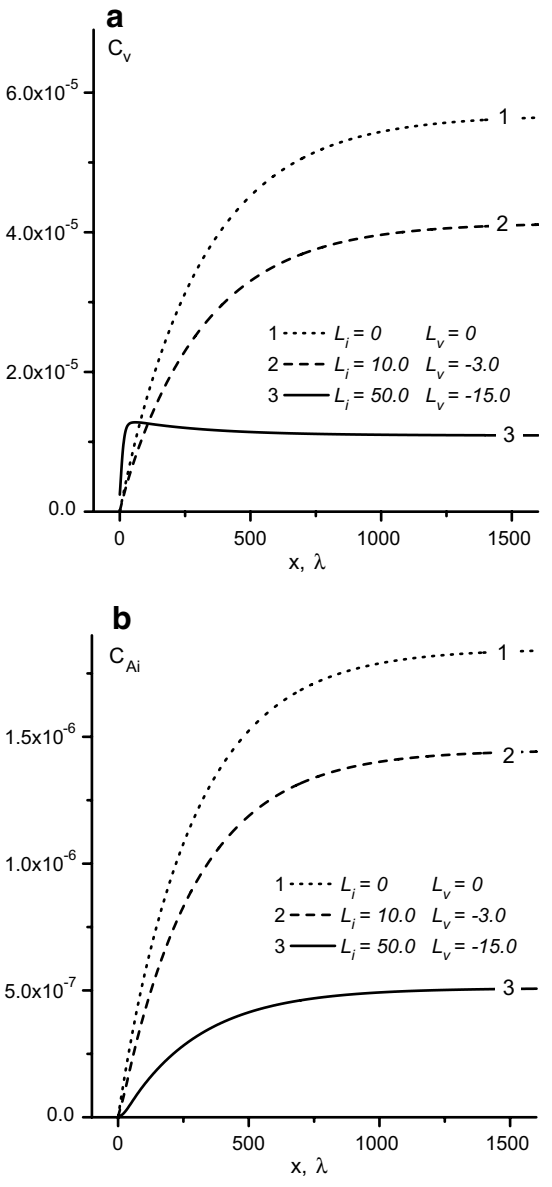

Fig. 2. Comparison of point defect profiles near a grain boundary: (a) for vacancies and (b) for interstitials at critical temperature obtained without effect of elastic stress field (curve 1), and taking into account this effect with different interaction energies for point defects (curves 2 and 3).

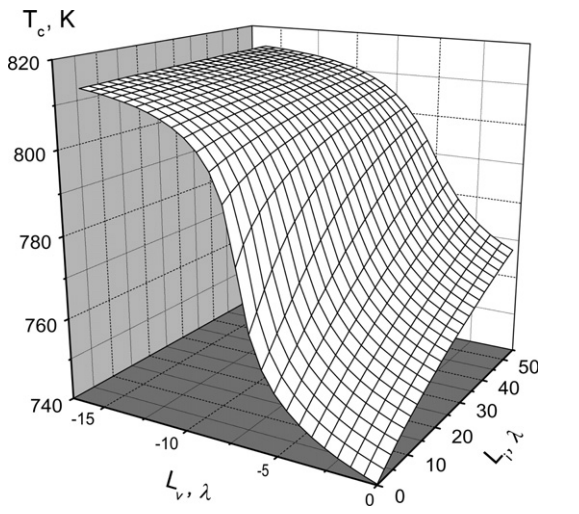

Fig. 3. Effect of the elastic stress field near grain boundary on the critical temperature for segregation reversal.

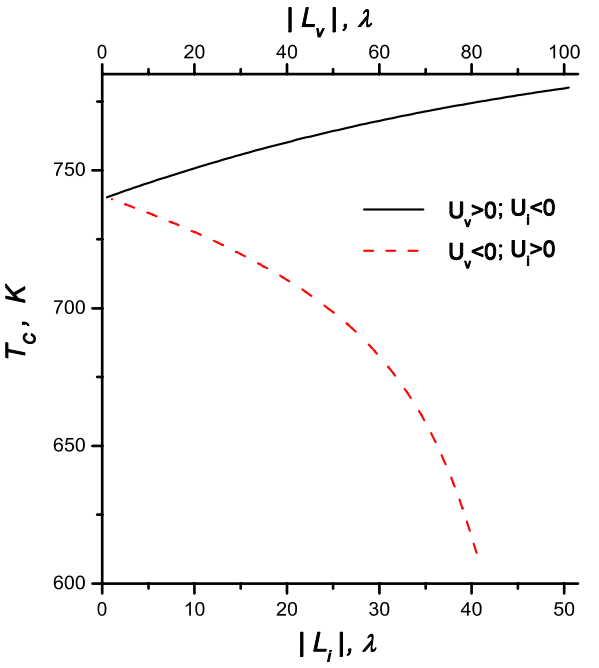

Fig. 4. Comparison of the critical temperatures for segregation reversal for opposite signs of the elastic stress field.

$\eta_B = 1$). Therefore the dependence of the critical temperature on elastic field parameters (Fig. 3.) is saturated in this region at high temperatures.

It should be noted that in the case of the opposite sign of the elastic interaction energy (11) the elastic stress field has opposite action on the critical temperature (Fig. 4). If the temperature lies between the critical values for the opposite signs of the elastic energy (10), a fluctuating segregation distribution can be observed.

4. Conclusions

It is shown that the elastic stress field near a grain boundary can change the profiles for radiation induced segregation. Elastic stress fields result in also a modification of point defect profiles and of their diffusion currents to a grain boundary. The current induced by the stress field will dominate and determine the direction of RIS near a grain boundary. This current in turn will be determined by drift rather than diffusion of point defects. Thus the balance of atomic currents will be shifted and the critical temperature T_c, the quantitative criterion for RIS direction, can be changed within a few tens of degrees, depending on values for stress field parameters. So, when L_v changes from 0 to -15 and L_i from 0 to 50, T_c is changed by 80° (see Fig. 3).

References

[1] J.R. Manning, Diffusion Kinetics for Atoms in Crystals, Van Nostrand, Princeton, 1968.
[2] R.A. Johnson, N.Q. Lam, Phys. Rev. B 13 (1976).
[3] H. Wiedesich, P.R. Okamoto, N.Q. Lam, J. Nucl. Mater. 83 (1979) 98.
[4] P.R. Okamoto, L.E. Rehn, J. Nucl. Mater. 83 (1979) 2.
[5] S. Watanabe, N. Sakaguchi, N. Hashimoto, H. Takahashi, J. Nucl. Mater. 224 (1995) 158.
[6] A.E. Volkov, A.I. Ryazanov, J. Nucl. Mater. 256 (1998) 108.
[7] M.V. Sorokin, A.E. Volkov, J. Nucl. Mater. 282 (2000) 47.
[8] M.V. Sorokin, A.E. Volkov, J. Nucl. Mater. 295 (2–3) (2001) 290.
[9] J.P. Hirth, J. Lothe, Theory of Dislocations, McGraw-Hill Book Company, New York, 1972.
[10] R.B. Nicholson, Phase Transformations, American Society for Metals, Metals Park, Ohio, 1968, p. 269.
[11] T.R. Anthony, Radiation-Induced Voids in Metals, in: J.W. Corbett, N.C. Ianniello (Eds.), US Atomic Energy Commission, Albany, New York, 1972, p. 630.
[12] S. Watanabe, N. Sakaguchi, S. Mochizuki, H. Takahashi, Philos. Mag. Let. 84 (5) (1996) 351.