Effect of point defect interaction with bubble surface on the nucleation and growth of gas bubbles

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Abstract

The influence of absorption ability of gas bubble surface on bubble kinetics in supersaturated solid solution of vacancies self-interstitial and gas atoms is investigated. Depending on the peculiarities of point defect absorption/desorption at the bubble surface possible cases of gas bubble ensemble kinetics are described. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 61.80.Az; 05.40.+j; 05.70.Fh

1. Introduction

Decay of supersaturated multi-component solid solutions results in nucleation and growth of a new phase that is determined by both stochastic microscopical processes of absorption/desorption of point defects and impurity atoms at the surface of nucleus and their diffusion from the bulk of material to the nucleus [1].

The precipitation kinetics are usually described in terms of the temporal and spatial dependent distribution function of nuclei sizes. Often the distribution function can be written down in the form of expansion into series where the zero order term represents the function that provides the detailed balance [1] in the phase space [1–4]. In the framework of (quasi) thermodynamic approach it is suggested that the function of detailed balance coincides with that of thermal fluctuations of nuclei sizes or its modification [3,4]. However, precipitation of a new phase can lead to non-uniform spatial distribution of point defects and impurity atoms in the vicinity of nuclei

(see e.g. [5]). Even in the case of one-component solid solution formation of the concentration profile can lead to discrepancy of the distribution function resulting in the detailed balance from that of thermal fluctuations of nuclei sizes [6,7]. In the general case of multi-component solid solution it is impossible to obtain the distribution function of the detailed balance if the additional 'potential' conditions [1] that relate the probabilities of absorption/evaporation of point defects and/or impurity atoms at the nuclei surface with each other are not fulfilled. Because the potential conditions usually are not accomplished, application of the analytical techniques based on the usage of the distribution function of the detailed balance can lead to divergence with the actual behaviour of the system especially when the concentration profiles exist [8,9].

In order to describe the evolution of a multi-component system complicated numerical techniques are also applied [10]. Drawbacks of these approaches are not only high computer resources requirements but mainly the crucial effect of the model form of the absorption/desorption probabilities of the components at the surface of the nuclei on the obtained results [10].

There are a number of less powerful and informative but simpler analytical techniques that can be applied for the description of precipitation in a supersaturated solid solution. One of these approaches is the nodal lines formalism [11,12] where one can qualify the kinetics of

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[1] The detailed balance corresponds to the zero current of bubbles in any point of the phase space [1].

the nuclei ensemble through the investigation of the arrangement of 'critical' points in the phase space [13,14]. Because the interaction of point defects and impurity atoms with nuclei surface affects the kinetic coefficients governing the arrangement of the critical points, the contribution of the surface kinetics to the precipitation can be investigated in the framework of the nodal lines formalism.

Among a great variety of multi-component systems the solid solution supersaturated with point defects and gas atoms attracts the special attention and is subjected to intensive investigations [5–21]. It is important for both practical and fundamental purposes. The relevant problem of radiation swelling is treated during the development of structural reactor materials. On the other hand, decay of supersaturated solid solution of vacancies, self-interstitial and gas atoms is an attractive model system for study of multi-component phase transition of the first order.

In the present paper the influence of peculiarities of point defect absorption/desorption at the bubble surface on the growth kinetics of the bubble ensemble is investigated in detail. In order to take into account these peculiarities the additional barriers for both gas atoms and point defects absorption/desorption at the bubble surface are introduced [9,22,23]. The approach aimed to reveal the cases when the microscopical features of the bubble surface kinetics significantly affect the ensemble evolution.

2. Formulation of the problem

Let us first formulate the kinetics of precipitation in three-component supersaturated solid solution. The solid solution is characterized by the corresponding concentrations $c_{\alpha\infty}$ ($\alpha = \alpha_1, \alpha_2, \alpha_3$ denotes the components) far from the precipitate. It is assumed that all the precipitates have spherical form.

Provided the average precipitate radius is less than the inter-precipitate distance and an diffusion interaction between precipitates can be neglected the kinetics of precipitation can be described by the distribution function of precipitate sizes $f(\mathbf{q}, t)$, where $\mathbf{q} = (\alpha_1, \alpha_2, \alpha_3)$ defines the phase space. So, $f(\mathbf{q}, t)\,d\mathbf{q}$ represents the volume density of nuclei with dimensions $\mathbf{q} \div \mathbf{q} + d\mathbf{q}$ in time t. We assume that the concentration of complexes of the solid solution components is negligible and therefore the evolution of the ensemble of precipitates occurs via constituent atoms absorption/desorption at the nuclei surface and the distribution function is evaluated from the Fokker–Plank equation [1]:

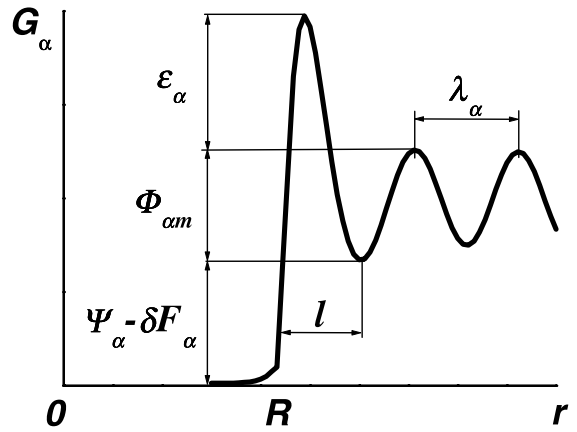$$\frac{\partial f}{\partial t} = -\nabla_{\mathbf{q}}\mathbf{J}, \tag{1}$$

Fig. 1. The Gibbs energy of the system containing the gas bubble of size (x, n) and an α-kind defect via positions of this defect from the bubble surface. ($\delta F = (\partial F_b/\partial x_\alpha) + (\partial F_s/\partial x_\alpha)$).

where

$$\mathbf{J} = \mathbf{A}f - \nabla_{\mathbf{q}}\left(\hat{\mathbf{B}}f\right). \tag{2}$$

Here $\mathbf{A} = (A_{\alpha_1}, A_{\alpha_2}, A_{\alpha_3})$ and $\hat{\mathbf{B}}_{ij}$, $i, j = \alpha_1, \alpha_2, \alpha_3$ are the kinetic coefficients.

The coefficients A_α, $\alpha = \alpha_1, \alpha_2, \alpha_3$ define 'hydrodynamic' rates of nuclei in the phase space. The coefficients B_{ij}, $i, j = \alpha_1, \alpha_2, \alpha_3$ define the stochastic ('diffusion') change of nuclei size and dominate in the vicinity of the critical point $\mathbf{q}_c$, where $\mathbf{A}(\mathbf{q}_c) = \mathbf{0}$, so that the ratio $|\mathbf{A}|/Sp\hat{\mathbf{B}} \ll 1$ is fulfilled. Determination of the kinetic coefficients A_α and B_{ij} fully qualifies the nucleation and growth kinetics of ensemble of precipitates [1].

An analysis of the kinetic coefficients A_α allows to deduce general peculiarities of evolution of ensemble of precipitates [13]. General form of the kinetic coefficients A_α have been obtained recently taking accurately into account the microscopic processes of the constituent atoms interaction with nucleus surface [9]

$$A_\alpha = \frac{4\pi R^2 l \xi}{\omega} \frac{Y_\alpha D_\alpha \exp(-\varepsilon_\alpha/T)}{\lambda_\alpha^2 + Rl\xi \exp(-\varepsilon_\alpha/T)}\left[c_{\alpha\infty} - C_{eq,\alpha}(R, \mathbf{q})\right]. \tag{3}$$

Here $D_\alpha = D_0 \exp(-\Phi_{\alpha m}/T)$ is the diffusion coefficient of species ($\alpha = \alpha_1, \alpha_2, \alpha_3$); $\Phi_{\alpha m}$ is the Gibbs energy barrier for the diffusion of the corresponding component in the matrix; T is the temperature in energy units; ω is the volume of matrix atom; λ_α is the corresponding diffusion jump length in matrix; ε_α is the additional barrier [2] (see Fig. 1) resulting from possible topological and

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[2] Actually these barriers define the ability of nucleus surface to absorb constituent atoms.

configurational peculiarities as well as matrix distortion and roughness of the precipitate surface [22,23]; R is the radius of a precipitate; ξ takes into account a number of evaporation sites in the surface layer; $Y_\alpha(R)$ are the bias factors taking into consideration the interaction of atoms of type α ($\alpha = \alpha_1, \alpha_2, \alpha_3$) with the elastic field of the precipitate [10,26]; $C_{\mathrm{eq},\alpha}(R, \mathbf{q})$ is the corresponding equilibrium concentration in the layer of thickness l at the bubble surface

$$C_{\mathrm{eq},\alpha}(R, \mathbf{q}) = C_{\mathrm{eq},\alpha}^0 \exp\left\{ -\frac{[(\partial F_\mathrm{b}/\partial \alpha) + (\partial F_\mathrm{s}/\partial \alpha)]}{T} \right\}.$$

Here $C_{\mathrm{eq},\alpha}^0 = \exp(-\Psi_\alpha/T)$ is the corresponding equilibrium concentration at the plain surface, Ψ_α is the corresponding energy of dissolution of the component α, ($\alpha = \alpha_1, \alpha_2, \alpha_3$) in matrix; $F_\mathrm{b}(\mathbf{q})$ and $F_\mathrm{s}(\mathbf{q})$ are the free energy of the species in the volume of precipitate and the free energy of the precipitate surface, respectively.

It seems that ensemble of gas bubbles in a material subjected to irradiation represents a system that can be treated in the framework of the formalism described above because three components of the supersaturated solid solution, namely vacancies (v), self-interstitial atoms (i) and gas atoms (x), are involved in evolution of gas bubble ensemble. However, the presence of both vacancies and self-interstitial atoms extracts the problem of decay of this multi-component solid solution into a special kind one. First of all, it is clear that the process of vacancy absorption (desorption) as well as self-interstitial atom desorption (absorption) results in the same change of the bubble volume. Indeed, a bubble volume, $V = 4\pi R^3/3$ is evaluated from

$$V = \omega_x x + \omega v + (-\omega)i = \omega_x x + \omega n, \quad n = v - i, \quad (4)$$

where ω_x is an increase of the bubble volume due to absorption of gas atom dissolved in matrix. Moreover, it is impossible to determine the absolute number of absorbed/evaporated vacancies and/or interstitial atoms because pairs (v_1, i_1) and (v_2, i_2) represent the same cavity provided $v_1 - i_1 = v_2 - i_2$. So, three-dimensional problem (x, v, i) of decay of supersaturated solid solution should be reduced to quasi-two-dimensional one (x, n), where the resulting vacancy flux (denoted with n) to the bubble comes from the difference of the actual vacancy current and the current of self-interstitial atoms from the bulk of material that results in the following formal kinetic coefficient A_n:

$$A_n = A_v - A_i$$

$$= \frac{4\pi R^2 l \xi}{\omega} \frac{Y_v D_v \exp(-\varepsilon_v/T)}{\lambda_v^2 + R l \xi \exp(-\varepsilon_v/T)} \left[c_v^{\mathrm{eff}} - C_{\mathrm{eq},v}(R, x, n) \right], \quad (5)$$

where

$$c_v^{\mathrm{eff}} = \left[1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \frac{Y_i(R)}{Y_v(R)} \frac{\lambda_v^2 + R l \xi \exp(-\varepsilon_v/T)}{\lambda_i^2 + R l \xi \exp(-\varepsilon_i/T)} \right.$$
$$\left. \exp\left(-\frac{\varepsilon_i - \varepsilon_v}{T} \right) \right] c_{v\infty} \quad (6)$$

is the 'effective' vacancy concentration (see also [4]) that can be either positive or negative. The case of negative c_v^{eff} corresponds to effective supersaturation with self-interstitial atoms and is not discussed here. The kinetic coefficient A_n has been evaluated under assumption of zero equilibrium concentration of self-interstitial atoms at the bubble surface ($C_{\mathrm{eq},i}(R) = 0$). Because below we emphasize the effects of the barriers ε_α on the bubble kinetics, it is assumed that all the biases are equal to unity ($Y_\alpha(R) = 1$). For application important cases [24,25] point defect recombination can be neglected.

It should be pointed out that performed analytical transformations demonstrate an important feature of phase transitions in solids with point defects. Particulary, general theory [1] of the multi-component transformation of the first order determines the critical nuclei ($\alpha_{1c}, \alpha_{2c}, \alpha_{3c}$) as the solution of the following equation set:

$$\begin{cases} A_{\alpha_1}(\alpha_{1c}, \alpha_{2c}, \alpha_{3c}) = 0 \\ A_{\alpha_2}(\alpha_{1c}, \alpha_{2c}, \alpha_{3c}) = 0, \\ A_{\alpha_3}(\alpha_{1c}, \alpha_{2c}, \alpha_{3c}) = 0 \end{cases} \quad (7)$$

whereas in our case the quite different condition is applied:

$$\begin{cases} A_x(x_c, n_c) = 0, \\ A_n(x_c, n_c) = A_v(x_c, v, i) - A_i(x_c, v, i) = 0. \end{cases} \quad (8)$$

It means that in the case of phase transformations of the first order in solids with point defects a 'dynamic' equilibrium can arise and the actual equilibrium state of the ensemble could not be described by the thermodynamic concept [4].

3. Effect of the bubble surface kinetics on the evolution of gas bubble ensemble

The analytical expressions for vacancy growth rate of gas bubbles, number of vacancies and gas atoms in the critical nuclei and critical gas bubble [13], etc. involve the effective vacancy concentration. Therefore the 'surface' term

$$\frac{\lambda_v^2 + R l \xi \exp(-\varepsilon_v/T)}{\lambda_i^2 + R l \xi \exp(-\varepsilon_i/T)} \exp\left(-\frac{\varepsilon_i - \varepsilon_v}{T} \right)$$

in Eq. (6) significantly affects the kinetics of gas bubble ensemble.

Depending on the bubble size, diffusion jump lengths λ_i and λ_v and the magnitudes of the barriers ε_i and ε_v the

following kinetic modes of gas bubble ensemble can be marked out:

1. Absorption kinetics of both vacancies and self-interstitial atoms is determined by their diffusion from the bulk of material (diffusion controlled case)

$$\frac{\lambda_\alpha^2}{R l \xi \exp(-\varepsilon_\alpha/T)} \ll 1 \ (\alpha = i, v). \tag{9}$$

The effective vacancy concentration c_v^{eff} and the growth rate $A_n(x, n)$ take the following forms:

$$c_v^{\text{eff}} = \left(1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}}\right) c_{v\infty} \equiv c_{v\ \text{dcc}}^{\text{eff}}, \tag{10}$$

$$A_n^{(d)}(x, n) = \frac{4\pi R}{\omega} D_v \left[c_v^{\text{eff}} - C_{\text{eq},v}(R, x, n)\right], \tag{11}$$

respectively. The spatial concentration profiles of point defects arise, see Fig. 2; the effect of the additional barriers ε_α ($\alpha = i, v$) on the growth of gas bubbles is absent in this case. The potential conditions [1] are not fulfilled and the distribution function of detailed balance in the diffusion controlled case does not exist [8,9]. So, the approaches based on the thermodynamic consideration as well as the methods utilizing the distribution function of detailed balance for the problem treatment can lead to uncertain results.

2. Absorption kinetics of both vacancies and self-interstitial atoms is determined by their interaction with surface of the bubble (reaction controlled case)

$$\frac{\lambda_\alpha^2}{R l \xi \exp(-\varepsilon_\alpha/T)} \gg 1 \ (\alpha = i, v). \tag{12}$$

In this case the effective vacancy concentration c_v^{eff} and growth rate $A_n(x, n)$ take the following forms:
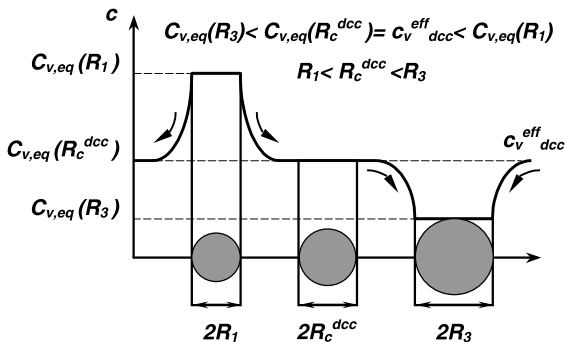

Fig. 2. 'Pure' diffusion controlled case. Concentration profiles of point defects in the vicinity of the bubbles arise. R_c^{dcc} denotes the radius of critical bubble in diffusion controlled case ($A_n(R_c^{\text{dcc}}) = 0$, $C_{v,\text{eq}}(R_c^{\text{dcc}}) = c_v^{\text{eff}}$ dcc). Gas bubbles with radius $R_1 < R_c^{\text{dcc}}$ are dissolved, whereas bubbles with radius $R_3 > R_c^{\text{dcc}}$ grow.

$$c_v^{\text{eff}} = \left(1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \left(\frac{\lambda_v}{\lambda_i}\right)^2 \exp\left(-\frac{\varepsilon_i - \varepsilon_v}{T}\right)\right) c_{v\infty}$$

$$\equiv c_{v\ \text{rcc}}^{\text{eff}} \tag{13}$$

$$A_n^{(r)}(x, n) = \frac{4\pi R}{\omega} D_v \frac{R l \xi \exp(-\varepsilon_v/T)}{\lambda_v^2}$$

$$\times \left[c_v^{\text{eff}} - C_{\text{eq},v}(R, x, n)\right]. \tag{14}$$

Eq. (13) shows that the barriers ε_α noticeably change the effective vacancy concentration $c_v^{\text{eff}} \equiv c_{v\ \text{rcc}}^{\text{eff}}$ provided $|\varepsilon_i - \varepsilon_v|/T \gtrsim 1$. The concentration $c_{v\ \text{rcc}}^{\text{eff}}$ is reduced ($c_{v\ \text{rcc}}^{\text{eff}} < c_{v\ \text{dcc}}^{\text{eff}}$) when $\varepsilon_i - \varepsilon_v < 0$, see Fig. 3(a), i.e., the process of vacancy absorption is less preferable than absorption of self-interstitial atoms. In the opposite case, the value of $c_{v\ \text{rcc}}^{\text{eff}}$ increases ($c_{v\ \text{rcc}}^{\text{eff}} > c_{v\ \text{dcc}}^{\text{eff}}$), see Fig. 3(b). One can see that at relevant temperatures $T \simeq 0.07$ eV (800 K) even small difference of additional diffusion barriers
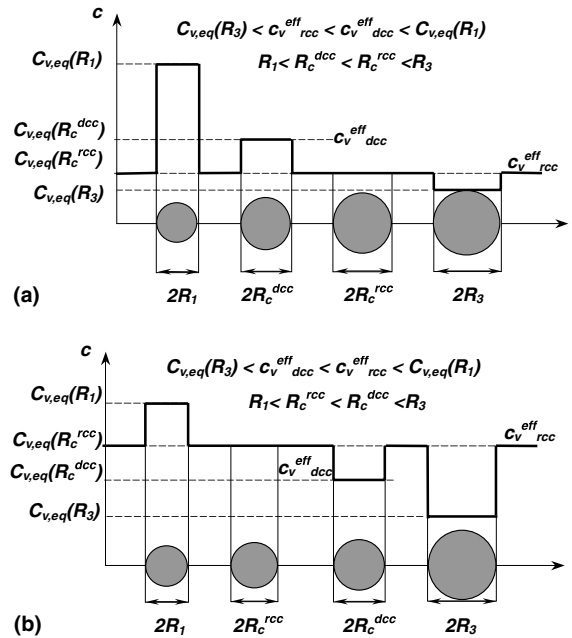

Fig. 3. Pure reaction controlled case. Nuclei do not perturb uniform distribution of point defects in their vicinity. Concentration step of point defects at a bubble surface appears. R_c^{rcc} denotes the radius of critical bubble in reaction controlled case ($A_n(R_c^{\text{rcc}}) = 0$, $C_{v,\text{eq}}(R_c^{\text{rcc}}) = c_{v\ \text{rcc}}^{\text{eff}}$). The effective vacancy concentration $c_{v\ \text{rcc}}^{\text{eff}}$ decreases (a) and increases (b) in comparison with that, $c_{v\ \text{dcc}}^{\text{eff}}$, in pure diffusion controlled case due to presence of the barriers ε_α ($\alpha = i, v$), see Eq. (13). In the former case ($\varepsilon_i - \varepsilon_v$) < 0 and the critical size shifts towards larger values ($R_c^{\text{rcc}} > R_c^{\text{dcc}}$), whereas in the latter case ($\varepsilon_i - \varepsilon_v$) > 0 the critical size shifts to smaller values ($R_c^{\text{rcc}} < R_c^{\text{dcc}}$). Gas bubbles with radius $R_1 < R_c^{\text{rcc}}$ are dissolved, whereas bubbles with radius $R_3 > R_c^{\text{rcc}}$ grow.

$|\varepsilon_v - \varepsilon_i| \sim 0.1$ eV can considerably change the effective concentration of vacancies and, hence, the gas bubble ensemble kinetics.

It should be also pointed out that presence of small term $Rl\xi \exp(-\varepsilon_v/T)/\lambda_v^2 \ll 1$ in Eq. (14) significantly reduces the magnitude of growth rate $A_n(x,n)$ in comparison with that for the diffusion controlled case (14) at the same c_v^{eff}.

3. Absorption of vacancies is determined by their diffusion from the bulk of material and absorption of self-interstitial atoms is determined by their interaction with the surface of the bubble

$$\frac{\lambda_v^2}{Rl\xi \exp(-\varepsilon_v/T)} \ll 1, \qquad \frac{\lambda_i^2}{Rl\xi \exp(-\varepsilon_i/T)} \gg 1. \quad (15)$$

In this case the effective vacancy concentration c_v^{eff} and growth rate $A_n(x,n)$ take the following forms:

$$c_v^{\mathrm{eff}} = \left(1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \frac{Rl\xi \exp(-\varepsilon_i/T)}{\lambda_i^2}\right) c_{v\infty}, \quad (16)$$

$$A_n(x,n) = \frac{4\pi R}{\omega} D_v \left[c_v^{\mathrm{eff}} - C_{\mathrm{eq},v}(R,x,n)\right], \quad (17)$$

respectively. Due to the small term $Rl\xi \exp(-\varepsilon_v/T)/\lambda_i^2 \ll 1$ in Eq. (16) the effective vacancy concentration c_v^{eff} is nearly equal to the vacancy concentration at infinity $c_{v\infty}$

$$c_v^{\mathrm{eff}} \simeq c_{v\infty}. \quad (18)$$

Absence of small terms in expression for vacancy growth rate (17) as well as Eq. (18) ensure facilitated nucleation and growth of gas bubbles in irradiated materials. In contrast to the previous 'pure' cases the effective vacancy concentration depends on the gas bubble radius in this case, see Fig. 4. Earlier it is

suggested that the effective vacancy concentration constitutes either the external parameter [8,9] or self-consistent ensemble dependent average [10] for the problem of gas bubble ensemble nucleation and growth. But according to Eq. (16) every gas bubble in ensemble has its *own* effective vacancy concentration. The dependence of c_v^{eff} on the bubble radius is crucial at large $D_i c_{i\infty}/D_v c_{v\infty}$ ratio.

4. Absorption of self-interstitial atoms is determined by their diffusion from the bulk of material and absorption of vacancies is determined by their interaction with the surface of the bubble:

$$\frac{\lambda_i^2}{Rl\xi \exp(-\varepsilon_i/T)} \ll 1, \qquad \frac{\lambda_v^2}{Rl\xi \exp(-\varepsilon_v/T)} \gg 1. \quad (19)$$

In this case the effective vacancy concentration c_v^{eff} and growth rate $A_n(x,n)$ have the following forms:

$$c_v^{\mathrm{eff}} = \left(1 - \frac{D_i c_{i\infty}}{D_v c_{v\infty}} \frac{\lambda_v^2}{Rl\xi \exp(-\varepsilon_v/T)}\right) c_{v\infty}, \quad (20)$$

$$A_n(x,n) = \frac{4\pi R}{\omega} D_v \frac{Rl\xi \exp(-\varepsilon_v/T)}{\lambda_v^2} \left[c_v^{\mathrm{eff}} - C_{\mathrm{eq},v}(R,x,n)\right], \quad (21)$$

respectively. Presence of small term $Rl\xi \exp(-\varepsilon_v/T)/\lambda_v^2 \ll 1$ in Eq. (20) as well as in Eq. (21) significantly reduce both the effective vacancy concentration c_v^{eff} and growth rate $A_n(x,n)$. That results in slow nucleation and growth of gas bubbles in irradiated materials in this case.

The effective vacancy concentration depends on the gas bubble size as well as in the previous case but in contrast to the last one c_v^{eff} increases with bubble radius increase, see Fig. 5.
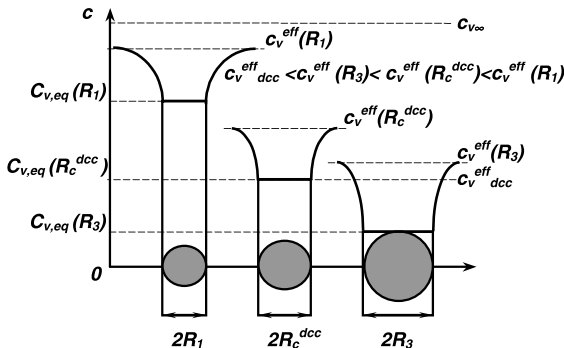

Fig. 4. Mixed case implementation. Concentration profile of vacancies in the vicinity of bubble exists, uniform distribution of self-interstitial atoms occurs. Every bubble has its *own* effective vacancy concentration. The effective vacancy concentration *decreases* with bubble radius increase; $c_{v\ \mathrm{dcc}}^{\mathrm{eff}} \leqslant c_v^{\mathrm{eff}}(R) \leqslant c_{v\infty}$, see Eq. (16).
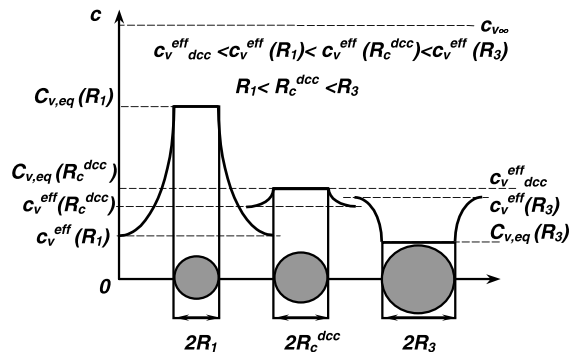

Fig. 5. Mixed case implementation, concentration profile of self-interstitial atoms arises, concentration step of vacancies occurs. Every bubble has its *own* effective vacancy concentration. The effective vacancy concentration *increases* with bubble radius increase; $c_v^{\mathrm{eff}}(R) \leqslant c_{v\ \mathrm{dcc}}^{\mathrm{eff}} \leqslant c_{v\infty}$ (see Eq. (20)).

4. Discussion

It has been found in previous section that depending on the values of the barriers ε_α $(\alpha = i, v)$ four limiting cases of deterministic evolution of gas bubble ensemble are possible. According to Eqs. (10) and (13) the effective vacancy concentration c_v^{eff} is independent on the size of the bubble when both vacancies and self-interstitial atoms absorption/desorption is defined by the same controlling case (either diffusion or reaction). We call these cases pure. Otherwise, the effective vacancy concentration c_v^{eff} depends on the bubble size, see Eqs. (16) and (20). These cases are called 'mixed'.

Kinetic coefficients A_n do not depend on the barriers ε_α $(\alpha = i, v)$ in the pure diffusion controlled case. However, range of applicability of the diffusion controlled case is governed by these barriers (see Fig. 6). Indeed, taking into account the expression for the volume of the bubble (4), one can see that the condition

$$\frac{\lambda_\alpha^2}{Rl\xi \exp(-\varepsilon_\alpha/T)} \gg 1 \tag{22}$$

is reduced to the following form (assuming λ_v, $\lambda_i = l$, $\xi = 1$):

$$x + n \ll \exp(3\varepsilon_\alpha/T) \quad (\alpha = i, v). \tag{23}$$

It is clear from (23) that if $\varepsilon_\alpha \leqslant 0$ for both vacancies $(\alpha = v)$ and self-interstitial atoms $(\alpha = i)$ the diffusion controlled case is realized in the whole phase space (x, n). Detailed balance cannot be achieved, so application of the techniques that uses the thermal fluctuations approach for description of the gas bubble ensemble nucleation and growth in this case can lead to doubtful results.

The positive values of the barriers ε_α $(\alpha = i, v)$ even slightly exceeded actual temperature (the relevant values are of the order of $T \sim 0.07$ eV) according to expression (23) significantly propagate the region in the dimension space where the reaction controlled case is realized. When the critical points of the gas bubble ensemble [11] [13] are covered by the reaction controlled case region (i.e., $x_c + n_c \ll \exp(3\varepsilon_\alpha/T)$), the influence of interaction of point defects with the bubble surface becomes crucial for the kinetics of gas bubble ensemble.

In the event of pure reaction controlled case the strong dependence of the effective vacancy concentration c_v^{eff} on the barriers values occurs (see Eq. (13)). Dependence of c_v^{eff} on $D_i c_{i\infty}/D_v c_{v\infty}$ ratio and $(\varepsilon_v - \varepsilon_i)/T$ is shown in Fig. 7. Several characteristic cross-sections of the surface in Fig. 7 are shown in Fig. 8. Analysis of Figs. 7 and 8 allows the following conclusions for the pure reaction controlled case to be drawn:

Fig. 7. Dependence of the effective vacancy concentration on $D_i c_{i\infty}/D_v c_{v\infty}$ ratio and $(\varepsilon_i - \varepsilon_v)/T$ for pure reaction controlled case.
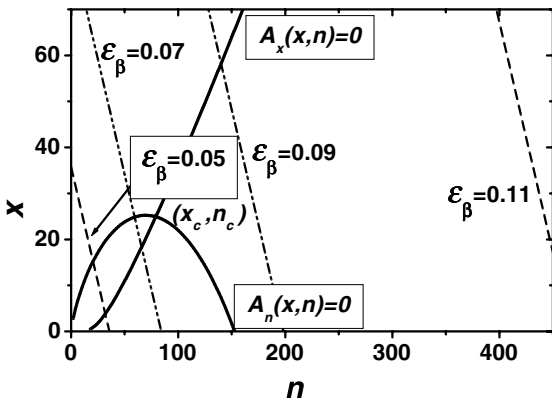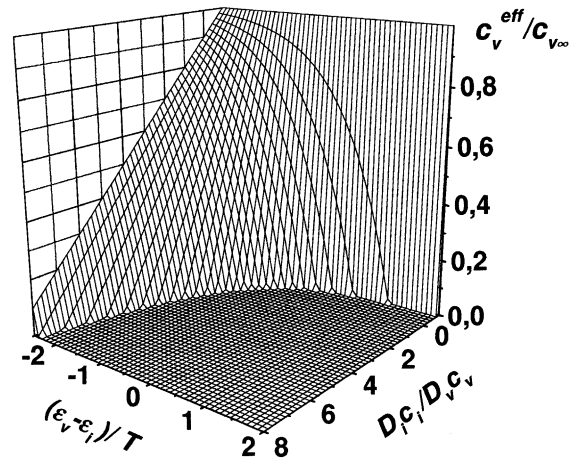

Fig. 6. Partitioning of the phase space into the regions with diffusion controlled (over straight line) and reaction controlled (below straight line) absorption/desorption of the point defects of type α at different values of the barrier ε_α (see. Eq. (23)).
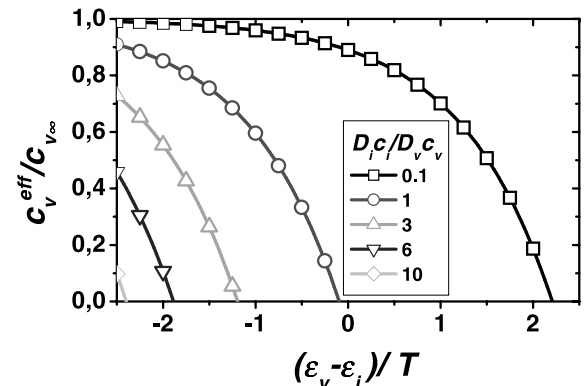

Fig. 8. Several cross-sections of the surface shown in Fig. 7.

- The nucleation and growth of gas bubble ensemble is possible even at $D_i c_{i\infty}/D_v c_{v\infty} > 1$ provided the ratio $(\varepsilon_i - \varepsilon_v)/T$ is positive and high enough, so as the following expression would be satisfied:

$$c_v^{\text{eff}} - C_{\text{eq},v}(R, x, n) > 0.$$

- The significance of the barriers ε_α increases with $D_i c_{i\infty}/D_v c_{v\infty}$ ratio increase. Strong dependence of the effective vacancy concentration on the ratio $(\varepsilon_i - \varepsilon_v)/T$ occurs at, respectively, large values of $D_i c_{i\infty}/D_v c_{v\infty}$ (when $D_i c_{i\infty}/D_v c_{v\infty} > 1$).

It should be pointed out that according to earlier investigations the condition $D_i c_{i\infty}/D_v c_{v\infty} > 1$ prohibits nucleation and growth of gas bubbles in the pure diffusion controlled case.

In order to illustrate the evolution of the ensemble of gas bubbles as a function of the effective vacancy concentration Figs. 9 and 10 are plotted. It is clear that the critical nucleus size rapidly decreases with c_v^{eff} increase. At the same time the change of the kinetic mode from gas driven ($A_x/A_n \ll 1$) to vacancy driven ($A_x/A_n \gg 1$) occurs [13,17].

Let us now discuss the mixed cases, when the spatial non-uniform distribution near the nucleus arises for one kind of point defects only (i.e., either for vacancies or self-interstitial atoms). Formation of diffusion profile of vacancies in the vicinity of gas bubbles (third case in Section 3) facilitates bubble growth provided the distribution of self-interstitial atoms is uniform (see Eq. (16)). Moreover no-barrier nucleation of gas bubbles can occur in this case, see Fig. 4. In the opposite case (fourth
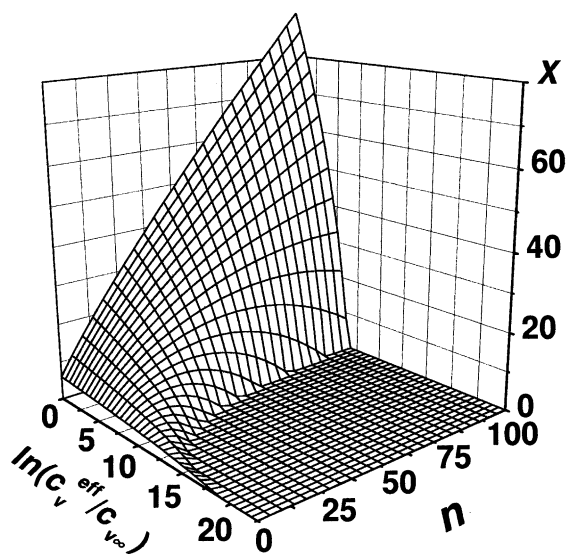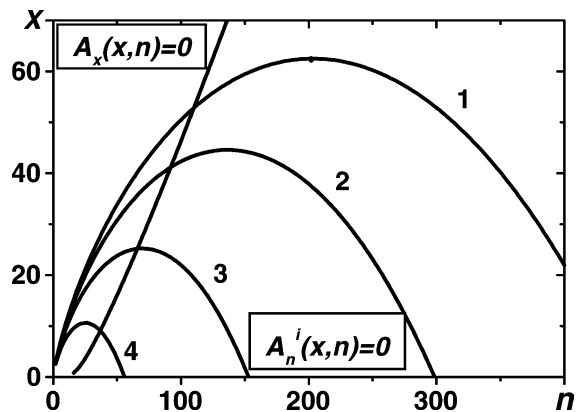
Fig. 10. Several cross-sections of the surface shown in Fig. 9. Curves 1 and 2 correspond to small effective supersaturation with vacancies when the number of vacancies in critical nucleus (x_c, n_c) is less than that in the maximum of the nodal line $A_n(x, n) = 0$. Helium induced nucleation of gas bubbles occurs in this case. Curve 3 corresponds to the case when the critical nuclei coincides with maximum of the nodal line $A_n(x, n) = 0$. Curve 4 is plotted for high effective supersaturation with vacancies. Helium assisted nucleation of gas bubbles occurs in this case.

case in Section 3) nucleation and growth of gas bubbles are suppressed (see Eqs. (20) and (21)).

Gas bubble in multi-component supersaturated solid solution with formed vacancy concentration profile and uniform distribution of self-interstitial atoms near bubbles (third case in Section 3) represents the system with degenerative feedback. Indeed the effective supersaturation with vacancies is reduced with increase of gas bubble radius, see Fig. 11(a), i.e., vacancy growth rate is reduced with bubble growth. In contrast, the case of suppressed nucleation of gas bubble ensemble (fourth case in Section 3) looks like the system with positive feedback, when the gas bubble radius increase leads to growth of the effective supersaturation with vacancies and therefore accelerates gas bubble growth, see Fig. 11(b).

5. Summary

The paper deals with surface kinetics influence on the nucleation and growth of gas bubble ensemble in solid solution supersaturated with vacancies, self-interstitial and gas atoms. It has been found that depending on the peculiarities of point defect interaction with surface of nucleus four limiting cases can be realized:

- Pure diffusion controlled case (non-uniform spatial distribution of point defects in the vicinity of gas bubble arises). Neither thermodynamic approaches

Fig. 9. The surface $A_n(x, n, c_v^{\text{eff}}) = 0$ in the case of pure reaction controlled case.

$$L_i = \frac{\lambda_i^2}{l\xi exp(-\varepsilon_i/T)}$$

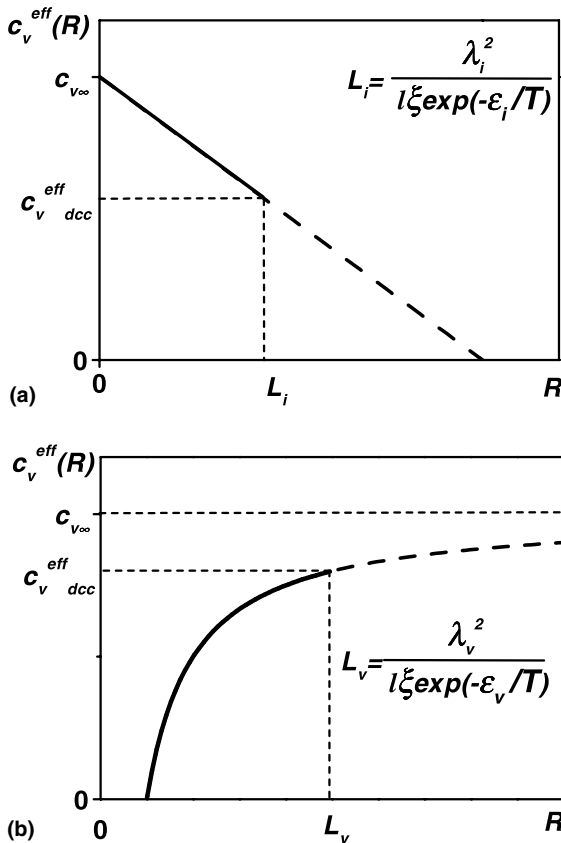$$L_v = \frac{\lambda_v^2}{l\xi exp(-\varepsilon_v/T)}$$

Fig. 11. Decrease of the effective vacancy concentration with bubble radius increase in the case of facilitated growth (third case in Section 3) (a) and increase of the effective vacancy concentration with bubble radius increase for suppressed evolution of gas bubbles (fourth case in Section 3) (b).

nor thermodynamic notions (e.g., the function of detailed balance) can be used for analytical consideration of the evolution of gas bubble ensemble. The condition $D_i c_{i\infty}/D_v c_{v\infty} > 1$ prohibits nucleation of gas bubbles. The effective vacancy concentration is independent of the barriers ε_α ($\alpha = i, v$).

- Pure reaction controlled case (concentration 'step' of point defects at the bubble surface occurs). The detailed balance of the system can be achieved and thermodynamic approaches can be applied for the analytical treatment of the system. The effective vacancy concentration (and hence the nucleation and growth kinetics) strongly depends on the barriers ε_α ($\alpha = i, v$). Negative difference ($\varepsilon_i - \varepsilon_v$) leads to shift of the critical nucleus towards the large values in the phase space, whereas the positive difference ($\varepsilon_i - \varepsilon_v$) results in the decrease of the critical size. In contrast to the pure diffusion controlled case the nucleation is possible even at $D_i c_{i\infty}/D_v c_{v\infty} > 1$ provided the difference ($\varepsilon_i - \varepsilon_v$) is high enough.

- Mixed cases (the spatial non-uniform distribution of either for vacancies or self-interstitial atoms near gas bubble arises). The effective vacancy concentration depends on the bubble radius, i.e., every gas bubble has its own effective concentration of vacancies. Provided the diffusion profile of vacancies arises in the vicinity of bubbles the facilitated nucleation and growth of gas bubbles occurs. The effective concentration of vacancies decreases with bubble radius increase in this case. Formation of diffusion profile of self-interstitial atoms results in suppressed nucleation and growth. However, the effective concentration of vacancies increases with bubble radius increase.

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