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DIFFUSION GROWTH AND MORPHOLOGICAL STABILITY OF TWO-DIMENSIONAL GRAIN BOUNDARY PRECIPITATES

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Diffusion growth of two-dimensional precipitates at the grain boundary of a finite thickness was considered with due regard to the diffusion fluxes of impurity atoms from the grain volume to the grain boundary. Stability of the growing precipitates of a relatively small radius was analyzed with respect to the small random perturbations of its size and subject to the surface kinetics of impurity atoms at the grain boundary/precipitate profile. Threshold radii of the precipitates, above which the amplitude of the shape defect and the amplitude of the relative shape deformation of the precipitates rise, were found.

Keywords: SUPERSATURATED SOLID SOLUTIONS, AGING METAL ALLOYS, REACTOR MATERIALS, RADIATION RESISTANCE, MACROSCOPIC INCLUSIONS, PRECIPITATES, GRAIN BOUNDARIES, DIFFUSION GROWTH, MORPHOLOGICAL STABILITY.

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1. INTRODUCTION

A great number of works (see, for example, monographs [1-5] and papers [6-12]) is devoted to the experimental and theoretical investigation of the behavior of macroscopic inclusions in real crystals. As known [1, 2, 4, 5], solid particles of the second phase, liquid inclusions, vacancy pores, and gas filled cavities belong to the macroscopic inclusions in crystalline matrix. Solid particles of the second phase are observed in composites, aging metal alloys [3, 9], decaying supersaturated solid solutions [2, 6-8].

It was discovered long ago that macroscopic inclusions, in particular, solid precipitates of a new phase are often formed at grain boundaries of polycrystals [1-8]. Such precipitates substantially influence the mechanical and other properties of macroscopic samples, in particular, the strengthening ones, the configuration of diffusion fluxes of impurity atoms or vacancies in the sample, the kinetics and rate of diffusion decay of the supersaturated solid solution.

In the theoretical description of the precipitates of a new phase, in many cases the following questions appear: nucleation of precipitates, their growth and size loss kinetics, their translation with regard to the grating due to the directional diffusion motion of atoms in the external force field, stability of their geometry, etc [1-12].

From the point of view of the radiation damage of reactor materials, presence of macroscopic inclusions influences their radiation resistance. In particular, precipitates of the second phase influence the dynamic balance of point defects in the material under irradiation due to the acceleration of the

point defect recombination at interphase boundaries, and, correspondingly, the swelling, distribution, and porosity parameters [5]. More specifically, precipitates of the second phase lead to the decrease in the average concentrations of point defects, and thereby, they impede nucleation and growth of vacancy pores [5]. When changing the precipitate morphology, their power as the point defect sink changes, and this, in turn, can influence behavior of the material under irradiation [5].

In the present work we theoretically consider diffusion growth of solid two-dimensional precipitate of a new phase at the grain boundary with a finite thickness δ by taking into account the surface growth kinetics on the lateral surface of precipitate and diffusion fluxes of impurity atoms from the grain volume to the grain boundary. Moreover, morphological stability of such precipitate is analyzed in linear approximation. High symmetry of the considered problem allows to obtain all final formulas in closed form that makes their physical analysis substantially easier.

2. MAIN CORRELATIONS

Diffusion equation of impurity atoms in the grain boundary, which is considered as a uniform isotropic layer with thickness δ [13-16], round precipitate of a new phase with regard to diffusion fluxes of impurity atoms from the grain volume to the grain boundary will be written in the form

$$\frac{\partial n_B}{\partial t} = D_B \Delta n_B + \frac{2I_V}{\delta}. \quad (1)$$

Here n_B is the volume density of impurity atoms in the grain boundary (two-dimensional density of impurity atoms is $n_S = n_B \delta$); D_B is the coefficient of the grain boundary diffusion, i.e. the volume diffusion coefficient of impurity atoms in the grain boundary (in the layer with thickness δ), I_V is the diffusion flux of impurity atoms from the grain volume to the grain boundary; factor 2 near I_V/δ takes into account bilateral diffusion supply of impurity atoms to the grain boundary.

We will consider plane cylindrical precipitate of a new phase with a constant height $h > \delta$ and base radius $R = R(t)$, which is crossed by the grain boundary, and plane faces of the precipitate are parallel to the grain boundary (see Fig. 1).

Flux of impurity atoms from the grain volume to the grain boundary in a steady (quasi-steady) state will be written in the form

$$I_V = D_V \frac{(\bar{n}_V - n_{VB})}{d/2}. \quad (2)$$

Here D_V is the diffusion coefficient of impurity atoms in the grain volume; d is the characteristic lateral grain size; \bar{n}_V is the density of impurity atoms in the grain volume; n_{VB} is the density of impurity atoms in the grain volume near the grain boundary. We assume that the grain size d considerably exceeds the precipitate sizes, i.e. $d \gg h$, $d \gg R$. We can neglect the change of the density n_B over the grain boundary thickness δ , as it is usually done [15, 16], if inequality $\delta^2/D_B \ll d^2/4D_V$ holds.

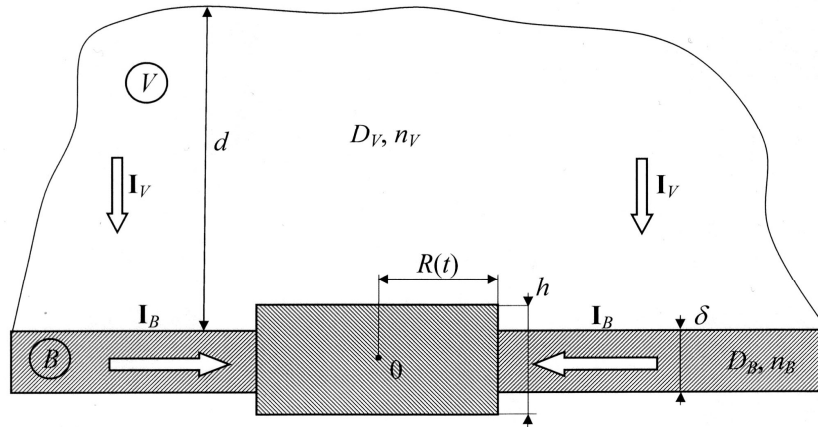


Fig. 1 – Schematic representation of plane cylindrical precipitate of a new phase placed on the grain boundary of a finite thickness δ . B is the grain boundary; V is the grain volume; I_B is the diffusion flux of impurity atoms in the grain boundary; n_V is the density of impurity atoms in the grain volume. Meaning of other notations is explained in the text

In the conditions of thermodynamic equilibrium, $n_{VB} \equiv n_{VB}^{\text{eq}}$ is found by equating the chemical potential of impurity atom in the grain volume near the grain boundary μ_{VB} and the chemical potential of impurity atom in the grain boundary μ_B ($\mu_{VB} = \mu_B$). In the approximation of weak solutions

$$\mu_{VB} = kT \ln(n_{VB}^{\text{eq}}/N_0) + \psi_V(P, T), \quad (3)$$

$$\mu_B = kT \ln(n_B/N_0) + \psi_B(P, T), \quad (4)$$

where k is the Boltzmann constant; N_0 is the density of lattice sites in the grain material; $\psi_{V,B}(P, T)$ are the functions depending on the pressure P and temperature T (see [17]). Finally, we obtain

$$n_{VB}^{\text{eq}} = C n_B, \quad C = \exp[(\psi_B - \psi_V)/kT]. \quad (5)$$

More general boundary condition for determination of the density n_{VB} , as well as the flux I_V (formula (2)), is formulated taking into account the surface kinetics of impurity atoms (see [2]) on the grain/grain boundary surface. Expression for the flux I_V in addition to the expression (2) will be written in the following form:

$$I_V = \beta_{VB}(n_{VB} - C n_B), \quad (6)$$

where β_{VB} is the surface kinetic coefficient on the grain/grain boundary surface, which characterizes the transition rate of impurity atoms from the grain volume into the grain boundary; $C n_B$ is the equilibrium value of the density n_{VB} (formula (5)). From equations (2) and (6) we find

$$I_V = \bar{D}_{VB} \frac{(\bar{n}_V - Cn_B)}{d/2}, \quad (7)$$

where

$$\bar{D}_{VB} \equiv \frac{D_V \beta_{VB} d/2}{D_V + \beta_{VB} d/2} \quad (8)$$

is the effective (with regard to the surface kinetics on the grain/grain boundary surface) diffusion coefficient of impurity atoms in the grain volume.

In quasi-steady approximation $\partial n_B / \partial t = 0$ (see [6]), and diffusion equation of impurity atoms in the grain boundary (1) with the flux I_V determined by formula (7) takes the form

$$\left(\frac{D_B}{4C\bar{D}_{VB}} d\delta \right) \Delta n_B + \frac{\bar{n}_V}{C} - n_B = 0. \quad (9)$$

We will assume that far from precipitate of a new phase the thermodynamic equilibrium between impurity atoms (which are in the grain volume near the grain boundary and in the grain boundary itself) exists. Then

$$\bar{n}_V = C\bar{n}_B, \quad (10)$$

where \bar{n}_B is the density of impurity atoms in the grain boundary far from precipitate of a new phase. Taking into account formula (10), equation (9) takes the form

$$L_B^2 \Delta n_B - n_B + \bar{n}_B = 0, \quad (11)$$

where

$$L_B \equiv \left(\frac{D_B}{4C\bar{D}_{VB}} d\delta \right)^{1/2} \quad (12)$$

is the typical length scale of the problem.

Boundary conditions for the equation (11) in the case of undistorted precipitate of a new phase in the form of circular cylinder are the following [18-21]:

$$D_B \frac{\partial n_B}{\partial r} \Big|_{r=R} = \beta_B [n_B(R) - n_{BR}], \quad n_B \Big|_{r \rightarrow \infty} \rightarrow \bar{n}_B. \quad (13)$$

Here r is the distance from the precipitate center in the grain boundary plane; n_{BR} is the thermodynamically equilibrium value of the density of impurity atoms in the grain boundary near the grain boundary/precipitate surface ($r = R$); β_B is the surface kinetic coefficient, which characterizes the transition rate of impurity atoms from the grain boundary into precipitate of a new phase. For the value of n_{BR} , the thermodynamic formula takes place

$$n_{BR} = n_{B\infty} \exp(\Gamma_B/R), \quad (14)$$

where $n_{B\infty}$ is the value of n_{BR} near plane grain boundary/precipitate surface ($R \rightarrow \infty$); $\Gamma_B \equiv \sigma_B \omega / kT$; σ_B is the specific interphase energy of the grain boundary/precipitate surface; ω is the volume per one impurity atom in precipitate. Further we will consider that the grain boundary is supersaturated by impurity atoms, i.e. $\bar{n}_B > n_{B\infty}$.

Solution of equation (11), which satisfies the boundary conditions (13), can be written as

$$\psi_B(r) = \psi_{BR} \frac{K_0(r/L_B)}{F_0(R/L_B)}. \quad (15)$$

Hereinafter $\psi_B(r) \equiv n_B(r) - \bar{n}_B$; $\psi_{BR} \equiv n_{BR} - \bar{n}_B$; $K_l(z)$ is MacDonald function of the l -th order [22],

$$F_0(z) \equiv K_0(z) + \frac{D_B}{\beta_B L_B} K_1(z). \quad (16)$$

Thermodynamically equilibrium density drop of impurity atoms in the grain boundary near precipitate of the radius R is the following:

$$\Delta n_{BR} \equiv (\bar{n}_B - n_{BR}) = n_{B\infty} [\exp(\Gamma_B/R^*) - \exp(\Gamma_B/R)] = -\psi_{BR}. \quad (17)$$

The critical precipitate radius

$$R^* = \frac{\Gamma_B}{\ln(\bar{n}_B/n_{B\infty})} \quad (18)$$

appears in formula (17) (precipitate with the radius $R > R^*$ grows up, and with the radius $R < R^*$ decreases in size).

3. DIFFUSION GROWTH RATE OF PRECIPITATE

Diffusion growth rate of precipitate is proportional to the diffusion flux of impurity atoms $\mathbf{I}_B = -D_B \nabla n_B$ on its lateral surface ($r = R$) and is found as

$$\frac{dR}{dt} = \frac{D_B \omega \delta}{h} \left. \frac{\partial n_B}{\partial r} \right|_{r=R} = \frac{D_B \omega \delta}{h} \left. \frac{\partial \psi_B}{\partial r} \right|_{r=R}. \quad (19)$$

Explicit expression for dR/dt follows from formulas (15), (17), (19) and is of the following form:

$$\frac{dR}{dt} = \frac{D_B \omega \delta}{h L_B} \frac{K_1(R/L_B)}{F_0(R/L_B)} \Delta n_{BR}. \quad (20)$$

If precipitate growth is limited by diffusion of impurity atoms ($D_B/\beta_B \rightarrow 0$), then

$$\frac{dR}{dt} = \frac{D_B \omega \delta}{h L_B} \frac{K_1(R/L_B)}{K_0(R/L_B)} \Delta n_{BR}. \quad (21)$$

If precipitate growth is limited by surface incorporation kinetics of impurity atoms into precipitate ($D_B/\beta_B \rightarrow \infty$), then

$$\frac{dR}{dt} = \frac{\beta_B \omega \delta}{h} \Delta n_{BR}. \quad (22)$$

Now consider other limiting cases of the general expression dR/dt (20). For precipitate of the sufficiently large radius ($R \gg L_B$) from formula (20) we obtain

$$\frac{dR}{dt} = \frac{\bar{D}_B \omega \delta}{h L_B} \Delta n_{BR}, \quad (23)$$

where

$$\bar{D}_B \equiv \frac{D_B \beta_B L_B}{D_B + \beta_B L_B} \quad (24)$$

is the effective (with regard to the surface incorporation kinetics) diffusion coefficient of impurity atoms in the grain boundary. For precipitate of a small radius ($R \ll L_B$) we have

$$\frac{dR}{dt} = \frac{D_B \omega \delta}{h} \frac{\Delta n_{BR}}{R K_0 (R/L_B) + D_B/\beta_B}. \quad (25)$$

We note that in the case $R \ll L_B$

$$K_0 (R/L_B) = -[\ln (R/2L_B) + \gamma] + O\left[(R/2L_B)^2 \ln (R/2L_B)\right], \quad (26)$$

where $\gamma = 0,5772\dots$ is the Euler constant [22].

Further, we will assume that radius of precipitate exceeds the critical one ($R > R^*$) that corresponds to the growth, not the decrease, of precipitate.

Growth time of precipitate from radius R_1 to radius R_2 in the quasi-steady approximation is found as follows (see formula (19)):

$$\Delta t (R_1, R_2) = \int_{R_1}^{R_2} \frac{dR}{(dR/dt)} = \frac{h}{D_B \omega \delta} \int_{R_1}^{R_2} \frac{dR}{\psi'_B (R)}, \quad (27)$$

where $\psi'_B (R) \equiv \left. \frac{d\psi_B (r)}{dr} \right|_{r=R}$.

At first, consider the case of small supersaturations of a solid solution of impurity atoms in the grain boundary

$$\Delta_B \equiv \frac{\bar{n}_B - n_{B\infty}}{n_{B\infty}} \ll 1. \quad (28)$$

In this case

$$\frac{\Gamma_B}{R^*} = \Delta_B \ll 1, \quad \frac{\Gamma_B}{R} < \frac{\Gamma_B}{R^*} \ll 1. \quad (29)$$

For precipitate of a small radius ($R \ll L_B$) at an arbitrary value of D_B/β_B , we write formula (25) with regard to (17) and (29) in the form

$$\frac{dR}{dt} = \frac{\Gamma_B D_B n_{B\infty} \omega \delta}{h (K_0 R + D_B/\beta_B)} \left(\frac{1}{R^*} - \frac{1}{R} \right), \quad (30)$$

where

$$K_0 \equiv K_0 (R/L_B). \quad (31)$$

Assuming that K_0 weakly (logarithmically) depends on the R (see formula (26)), from formulas (27) and (30) we find

$$\Delta t (R_1, R_2) = t_0 \left\{ \frac{u_2^2 - u_1^2}{2} + \left(1 + \frac{D_B/\beta_B}{K_0 R^*} \right) \left[(u_2 - u_1) + \ln \left(\frac{u_2 - 1}{u_1 - 1} \right) \right] \right\}, \quad (32)$$

where dimensionless initial and finite precipitate radii $u_1 \equiv R_1/R^*$ and $u_2 \equiv R_2/R^*$, respectively, are introduced, and

$$t_0 \equiv \frac{h K_0 R^{*3}}{\Gamma_B D_B n_{B\infty} \omega \delta} \quad (33)$$

is the typical time of diffusion change of the precipitate size.

For precipitate of a large radius ($R \gg L_B$) in the case of small supersaturations (28), (29), formulas (17), (23), and (27) give

$$\Delta t (R_1, R_2) = t_1 \left[(u_2 - u_1) + \ln \left(\frac{u_2 - 1}{u_1 - 1} \right) \right], \quad (34)$$

where

$$t_1 \equiv \frac{h L_B R^{*2}}{\Gamma_B \bar{D}_B n_{B\infty} \omega \delta}. \quad (35)$$

Comparison of formulas (22) and (23) shows: if precipitate growth is limited by surface incorporation kinetics of impurity atoms into precipitate (R is arbitrary, $\Delta_B \ll 1$), then formula (34) remains valid, and in formula (35) we should replace \bar{D}_B/L_B by β_B . In this case, precipitate, obviously, “does not feel” diffusion length of impurity atoms in the grain boundary, which is different for precipitates of small ($R \ll L_B$) and large ($R \gg L_B$) radii.

We note that in formulas (32) and (34) there is a term proportional to $\ln((u_2 - 1)/(u_1 - 1))$, i.e. $\Delta t(R_1, R_2)$ has logarithmic singularity at $R_1 \rightarrow R^*$ ($u_1 \rightarrow 1$). Presence of this divergence is connected with the fact that in the general case rate dR/dt (formula (20)) is proportional to Δn_{BR} (expression (17)) and goes to zero at $R = R^*$.

We will also present the growth times of precipitate in the case of large supersaturations of a solid solution of impurity atoms in the grain boundary ($\bar{n}_B \gg n_{BR}$).

1. Precipitate of a small radius ($R \ll L_B$), ratio D_B/β_B is arbitrary:

$$\Delta t(R_1, R_2) = \frac{hK_0R^{*2}}{D_B\bar{n}_B\omega\delta} \left[\frac{u_2^2 - u_1^2}{2} + \frac{D_B/\beta_B}{K_0R^*} (u_2 - u_1) \right]. \quad (36)$$

2. Precipitate of a large radius ($R \gg L_B$):

$$\Delta t(R_1, R_2) = \frac{hL_B R^*}{\bar{D}_B\bar{n}_B\omega\delta} (u_2 - u_1). \quad (37)$$

3. Precipitate growth is limited by surface incorporation kinetics of impurity atoms into precipitate, R is arbitrary:

$$\Delta t(R_1, R_2) = \frac{hR^*}{\beta_B\bar{n}_B\omega\delta} (u_2 - u_1). \quad (38)$$

We note that in the cases of (37) and (38) precipitate grows with a constant rate $dR/dt = \text{const}$.

4. LINEAR ANALYSIS OF THE MORPHOLOGICAL STABILITY OF PRECIPITATE

We will analyze the stability of a circular precipitate during its growth (the morphology stability) as it was performed for small islands under deposition of material on the crystal surface [20, 21]. Methods of such analysis with regard to the stability problems of a growth form are stated in a number of publications [23-29] starting from the classical work by Mullins and Sekerka.

Assuming that perturbation of a circular precipitate is small, we consider it as a superposition of circular harmonics $\exp(il\varphi)$, $l \geq 1$:

$$R(\varphi, t) = R(t) + \sum_{l \geq 1} \xi_l(t) \exp(il\varphi). \quad (39)$$

Here $R(\varphi, t)$ is the type of the perturbed precipitate boundary in the polar coordinate system with the origin in the precipitate center; l is the number of harmonic; ξ_l is the small perturbation amplitude corresponding to the l -th harmonic ($\xi_l \ll R$); φ is the polar angle. In (39) we neglect the precipitate-shape distortion, which is, in fact, the cylindrical one, $\sim \exp(iqz)$ along the cylinder axis z . Such neglect suggests that the precipitate height h , anyway, is substantially less than its radius R ($h \ll R$). Being limited only by the linear analysis of the stability, in further formulas we will omit the terms with $\xi_l/R \ll 1$ in the power higher the first one. Since all the problem equations are linear, it is enough to investigate the precipitate-shape distortion described by the single circular harmonic $\exp(il\varphi)$, not by their superposition $\sum_l \xi_l \exp(il\varphi)$.

Curvature of the precipitate boundary for the perturbation of the form $\xi_l \exp(il\varphi)$ is the following:

$$K = \frac{1}{R} + (l^2 - 1) \frac{\xi_l}{R^2} \exp(il\varphi), \quad (40)$$

where $1/R$ is the curvature value for the precipitate of undisturbed circular shape. Boundary condition, which is similar to the first one from conditions (13), should be written on the true, i.e. the disturbed precipitate boundary $R(\varphi, t) = R(t) + \xi_l(t)\exp(il\varphi)$. This condition has the following form:

$$D_B \frac{\partial n_B}{\partial r} \Big|_{r=R(\varphi,t)} = \beta_B [n_B - n_{B\infty} \exp(\Gamma_B K)]_{r=R(\varphi,t)}. \quad (41)$$

Solution of the diffusion equation of impurity atoms (11), which satisfies the condition (41) on the disturbed precipitate boundary and the condition $\psi_B \rightarrow 0$ at $r \rightarrow \infty$, can be written as

$$\psi_B(\rho, \varphi) = \psi_{BR} \frac{K_0(\rho)}{F_0(a)} + \left[\psi_{BR} \frac{F_1(a)}{F_0(a)} a + (l^2 - 1) \frac{\Gamma_B n_{BR}}{R} \right] \frac{K_l(\rho)}{F_l(a)} \frac{\xi_l}{R} \exp(il\varphi). \quad (42)$$

Here $\rho \equiv r/L_B$; $a \equiv R/L_B$; and the introduced functions $F_l(a)$ are defined by the correlations

$$F_l(a) \equiv K_l(a) + \frac{D_B}{\beta_B L_B} |K_l'(a)|. \quad (43)$$

Displacement velocity of the precipitate boundary (its r -th component) is

$$V_r = \frac{D_B \omega \delta}{h} \frac{\partial \psi_B}{\partial r} \Big|_{r=R(\varphi,t)}. \quad (44)$$

On the other hand, obviously,

$$V_r = \frac{\partial R(\varphi, t)}{\partial t} = \dot{R}(t) + \dot{\xi}_l(t) \exp(il\varphi). \quad (45)$$

Equating expression (44) with the obtained function $\psi_B(\rho, \varphi)$ (formula (42)) and expression (45), we find formula (20) for $\dot{R}(t) \equiv dR/dt$ and formula for the amplitude increment $\dot{\xi}_l(t)$

$$v_l \equiv \frac{d}{dt} \ln[\xi_l(t)] = \frac{\dot{\xi}_l}{\xi_l}, \quad (46)$$

$$v_l = \frac{D_B \omega \delta}{h L_B} \left[G_B \phi_l(a) - (l^2 - 1) \frac{\Gamma_B n_{BR}}{R^2} \frac{|K_l'(a)|}{F_l(a)} \right]. \quad (47)$$

Here

$$G_B \equiv \frac{\partial n_B}{\partial r} \Big|_{r=R} = \frac{\Delta n_{BR}}{L_B} \frac{K_1(a)}{F_0(a)} \quad (48)$$

is the density gradient of impurity atoms on the boundary of undisturbed precipitate;

$$\phi_l(a) \equiv \frac{F_l(a)}{K_1(a)} \frac{|K_l'(a)|}{F_l(a)} - \frac{|K_1'(a)|}{K_1(a)}. \quad (49)$$

Relative deformation of the precipitate shape is determined by the ratio ξ_l/R . Starting from the formulas (20), (46), (47), we write expression for the increment of ξ_l/R

$$\mu_l \equiv \frac{d}{dt} \ln \left[\frac{\xi_l(t)}{R(t)} \right] = \frac{\dot{\xi}_l}{\xi_l} - \frac{\dot{R}}{R}, \quad (50)$$

$$\mu_l = \frac{D_B \omega \delta}{h L_B} \left\{ G_B \left[\phi_l(a) - \frac{1}{a} \right] - (l^2 - 1) \frac{\Gamma_B n_{BR}}{R^2} \frac{|K_l'(a)|}{F_l(a)} \right\}. \quad (51)$$

Let us write and analyze the correlations (47) and (51) for the case of the precipitate with a sufficiently small radius ($R \ll L_B$)

$$\nu_l = (l-1) \frac{D_B \omega \delta}{h R} \frac{1}{1 + l D_B / \beta_B R} \left[G_B - l(l+1) \frac{\Gamma_B n_{BR}}{R^2} \right], \quad (52)$$

$$\mu_l = \frac{D_B \omega \delta}{h R} \frac{1}{1 + l D_B / \beta_B R} \left\{ \left[l \left(1 - \frac{D_B}{\beta_B R} \right) - 2 \right] G_B - l(l^2 - 1) \frac{\Gamma_B n_{BR}}{R^2} \right\}, \quad (53)$$

$$G_B = \frac{\Delta n_{BR}}{K_0 R + D_B / \beta_B}. \quad (54)$$

As seen from the formula (52), increment ν_l contains two terms of different physical nature. The first term proportional to the density gradient of impurity atoms G_B leads to the rise of the harmonic amplitude $\xi_l(t)$. This rise is connected with the fact that asperity on the boundary of growing precipitate has the possibility to "gather" more impurity atoms than surrounding segments of the boundary, and therefore it can advance precipitate during growth. The second term proportional to the specific interphase energy of the boundary σ_B ($\Gamma_B \sim \sigma_B$) leads to the decrease in the amplitude $\xi_l(t)$. Really, since asperities have higher densities of impurity atoms than hollows, there are fluxes of impurity atoms from asperities to hollows, which reduce the distortion amplitude smoothing the boundary. And question about the stability of circular precipitate boils down to the following: what effect is found to be stronger.

Factor $(l-1)$ in formula (52) leads to $\nu_l = 0$ at $l = 1$. This is connected with the fact that in the linear approximation over $\xi_l/R \ll 1$ the first perturbation harmonic ($l = 1$) just leads to the shift of a circle (precipitate boundary) by ξ_1 without distortion of the precipitate shape.

Condition of the l -th harmonic rise $\nu_l > 0$, which follows from formula (52), we will write in the form

$$G_B > l(l+1) \frac{\Gamma_B n_{BR}}{R^2} \quad (55)$$

or, taking into account formulas (14), (17), and (54)

$$\frac{R}{R^*} > l(l+1) \left(K_0 + \frac{D_B}{\beta_B R} \right) \frac{\exp(\Gamma_B/R)}{\exp(\Gamma_B/R^*) - \exp(\Gamma_B/R)} \frac{\Gamma_B}{R^*} \quad (56)$$

and we will consider $R > R^*$. Then at $R \rightarrow R^* + 0$ the right side of the inequality (56) infinitely increases due to the fact that denominator tends to $+0$, while its left side $R/R^* \rightarrow 1$, i.e. inequality (56) does not hold. This means that at $R \rightarrow R^* + 0$ the precipitate shape is stable, and instability of the circular precipitate can be only for some finite distance of R from R^* ($R > R^*$).

Let us find the nucleation threshold of such instability of the precipitate shape, i.e. the threshold precipitate radius $R_{C1}(l)$, above which $\xi_l(t)$ increases ($v_l > 0$, $l > 1$). For this, we will approximately solve the following equation:

$$\frac{R}{R^*} = l(l+1) \left(K_0 + \frac{D_B}{\beta_B R} \right) \frac{\exp(\Gamma_B/R)}{\exp(\Gamma_B/R^*) - \exp(\Gamma_B/R)} \frac{\Gamma_B}{R^*}, \quad (57)$$

which in the case of small supersaturations (28), (29) takes the form

$$\frac{R}{R^*} - 1 = l(l+1) \left(K_0 + \frac{D_B}{\beta_B R} \right). \quad (58)$$

Neglecting the dependence of K_0 on R , equation (58) is reduced to the quadratic one with respect to R , and its unique physical solution is the following:

$$R_{C1}(l) = \frac{1}{2} [l(l+1)K_0 + 1] R^* + \left\{ \frac{1}{4} [l(l+1)K_0 + 1]^2 + l(l+1) \frac{D_B}{\beta_B R^*} \right\}^{1/2} R^*. \quad (59)$$

As seen from formula (59), $R_{C1}(l)$ increases with the rise of l . Then instability of the circular precipitate during its growth occurs for the first time on the second harmonic ($l = 2$). The corresponding threshold radius is equal to

$$R_{C1}(2) = \left(3K_0 + \frac{1}{2} \right) R^* + \left[\left(3K_0 + \frac{1}{2} \right)^2 + \frac{6D_B}{\beta_B R^*} \right]^{1/2} R^*. \quad (60)$$

If the precipitate growth is limited by the diffusion of impurity atoms (i.e. $D_B/\beta_B \rightarrow 0$), formulas (59) and (60) take the form

$$R_{C1}(l) = [l(l+1)K_0 + 1] R^*, \quad (61)$$

$$R_{C1}(2) = (6K_0 + 1) R^*. \quad (62)$$

For the case of small supersaturations (28), (29), we will also find the threshold precipitate radius $R_{C2}(l)$, above which relative deformation of the precipitate shape ξ_l/R increases ($\mu_l > 0$). This radius is defined by the equation following from formulas (53) and (54)

$$\frac{R}{R^*} - 1 = \frac{l(l^2 - 1)}{l(1 - D_B/\beta_B R) - 2} \left(K_0 + \frac{D_B}{\beta_B R} \right). \quad (63)$$

Neglecting the dependence of K_0 on R , equation (63) at $l > 2$ is reduced to the quadratic one with respect to R

$$(l-2)R^2 - \left[l(l^2 - 1)K_0 R^* + (l-2)R^* + l \frac{D_B}{\beta_B} \right] R - l(l^2 - 2) \frac{D_B R^*}{\beta_B} = 0. \quad (64)$$

In the case $l = 2$, equation (64) has, obviously, unique negative root that is not physical. Thus, increase in the relative deformation of the precipitate shape ξ_l/R can occur starting from the third harmonic. Indeed, equation (64) has unique physical solution at $l \geq 3$

$$R_{C2}(l) = U_l R^* + (U_l^2 + V_l)^{1/2} R^*, \quad (65)$$

where

$$U_l \equiv l \frac{(l^2 - 1)K_0 + D_B/\beta_B R^*}{2(l-2)} + \frac{1}{2}, \quad (66)$$

$$V_l \equiv \frac{l(l^2 - 2)}{l-2} \frac{D_B}{\beta_B R^*}. \quad (67)$$

At $l = 3$ formulas (65)-(67) give

$$R_{C2}(3) = \left(12K_0 + \frac{1}{2} + \frac{3}{2} \frac{D_B}{\beta_B R^*} \right) R^* + \left[\left(12K_0 + \frac{1}{2} + \frac{3}{2} \frac{D_B}{\beta_B R^*} \right)^2 + 21 \frac{D_B}{\beta_B R^*} \right]^{1/2} R^*. \quad (68)$$

Now we raise a question about the most fast increasing perturbation harmonic of the circular precipitate at $R > R_{C1}(l)$. In the case $lD_B/\beta_B R \ll 1$, where $l \gg 1$ (developed instability), as it can be shown from formulas (17), (52), (54), for the number l^* of the most fast increasing harmonic and the corresponding harmonic wavelength $\lambda^* = 2\pi R/l^*$ the following formulas take place

$$l^* = \left[R \frac{\exp(\Gamma_B/R^*) - \exp(\Gamma_B/R)}{3 \exp(\Gamma_B/R) \Gamma_B K_0} \right]^{-1/2}, \quad (69)$$

$$\lambda^* = 2\pi \left[\frac{3 \exp(\Gamma_B/R) \Gamma_B K_0 R}{\exp(\Gamma_B/R^*) - \exp(\Gamma_B/R)} \right]^{1/2}. \quad (70)$$

In the case of small supersaturations (28), (29), formulas (69) and (70) give

$$l^* = \left(\frac{R/R^*}{3K_0} \right)^{1/2} \sim \left(\frac{R}{R^*} \right)^{1/2}, \quad (71)$$

$$\lambda^* = 2\pi (3K_0 R R^*)^{1/2} \sim (R R^*)^{1/2}. \quad (72)$$

The assumed condition $l^* \gg 1$ ($l^* > 10$), as it follows from (71), in the case of small supersaturations holds sufficiently well at $R/R^* > 1,5 \times 10^3$. Since harmonic with the number l^* is the most fast increasing harmonic of the arbitrary perturbation of the precipitate shape, the relative contribution of this harmonic into the series expansion of distortion (39) increases. Due to this fact, the wavy distortion with the wavelength $\sim \lambda^*$ will appear on the precipitate lateral surface.

5. CONCLUSIONS

Thus, we have theoretically considered diffusion growth of two-dimensional precipitate of a new phase at the grain boundary of a finite thickness δ with regard to diffusion fluxes of impurity atoms from the grain volume to the grain boundary. The growth rate of precipitate dR/dt (formulas (19)-(25)) is defined in different limiting cases for arbitrary supersaturations of a solid solution of impurity atoms in the grain boundary Δ_B . The growth time of precipitate from radius R_1 to radius R_2 $\Delta t(R_1, R_2)$ (formula (27)) is obtained both in the case of small supersaturations (formulas (32)-(35)) and in the case of large supersaturations (formulas (36)-(38)).

We have also carried out the linear analysis of the stability of circular precipitate of a small radius ($R \ll L_B$) during its growth ($R > R^*$) with respect to small arbitrary perturbations of its shape $\sum_l \xi_l \exp(il\varphi)$, $\xi_l \ll R$ (formula (39)) subject to the surface kinetics of impurity atoms on the precipitate lateral surface (boundary condition (41)). The discussed further results (if other is not mentioned) are obtained in the case of small supersaturations of a solid solution of impurity atoms in the grain boundary ($\Delta_B \ll 1$).

The threshold precipitate radii $R_{C1}(l)$, $R_{C2}(l)$, above which, respectively, the amplitude of the shape perturbation ξ_l/R (formula (59)) and the amplitude of the relative shape deformation $\xi_l(t)/R(t)$ (formulas (65)-(67)) of the precipitates rise, are determined. Instability of circular precipitate for an arbitrary value of D_B/β_B occurs for the first time on the second harmonic ($l = 2$), the corresponding threshold radius $R_{C1}(2)$ is given by the formula (60). Increase in the relative shape deformation ξ_l/R begins on the third harmonic ($l = 3$), the value of $R_{C2}(3)$ is defined by the formula (68). As follows from formulas (59), (65)-(67), rise of the importance of the surface kinetics in the impurity atom transport to the precipitate (increase in the ratio D_B/β_B) leads to the increase in the threshold radii $R_{C1}(l)$ and $R_{C2}(l)$.

The number of the most fast increasing harmonic l^* (formula (69)) and the corresponding harmonic wavelength λ^* (formula (70)) are obtained in the case of the developed shape instability of the precipitate (instability on the harmonics with the numbers $l \gg 1$) at arbitrary supersaturations of a solid solution of impurity atoms in the grain boundary Δ_B . Here we assumed that $lD_B/\beta_B R \ll 1$. In the case of small supersaturations ($\Delta_B \ll 1$), l^* and λ^* are represented by the formulas (71) and (72), respectively.

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