Ostwald Ripening of Diffusion-Limited Small-Size Precipitates at Grain Boundaries

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The paper describes a theoretical study of the Ostwald ripening of two-dimensional small-size precipitates of a newly formed phase at the grain boundary of finite thickness, taking into account the diffusion of impurity atoms from the grain interior to the grain boundary. The precipitate growth is believed to be limited by the impurity-atom diffusion in the grain boundary. The asymptotic time dependences are found for the average critical precipitate radius, supersaturation of solid solution of impurity atoms in the grain boundary, precipitate size distribution function, precipitate density, and for the factor of grain boundary filling with precipitates. A discussion of the limits of validity of the obtained results is given.

**Keywords:** Supersaturated Solid Solutions, Diffusion Decomposition, Precipitates, Ostwald Ripening, Real Crystals, Macrodefects, Grain Boundaries, Grain Boundary Diffusion, Aged Metal Alloys, Reactor Constructional Materials, Radiation Strength, Diffusion Growth, Vacancy Pores.

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1. **INTRODUCTION**

Three stages are distinguished during diffusion decomposition of supersaturated solid solution which occurs by the fluctuation formation and further growth of discrete regions (centers) of a new phase (nuclei of a new phase) [1-9]. On the initial stage of decomposition, when supersaturation of solid solution by impurity atoms is sufficiently high, intensive formation of viable nuclei of a new phase with sizes larger than the critical one (supercritical nuclei) takes place. A number of impurity atoms in nuclei is still small on the initial stage in comparison with the amount contained in solid solution, and supersaturation of solid solution was not able to be decreased significantly.

On the second stage, a number of impurity atoms in nuclei is comparable with that contained in solid solution; here, supersaturation starts decaying. Amount of nuclei on this stage is weakly changed, and fraction of a new phase increases, mainly, due to the growth of the present viable nuclei.

The third, later stage of diffusion decomposition was discovered by Ostwald in 1900 [10]. On this stage, supersaturation becomes very small, and fluctuation formation of new nuclei does not almost occur, since they have macroscopically large sizes. Increase in the critical size of a nucleus connected with the decrease in the solution supersaturation leads to the fact that smaller centers of a new phase which were formed pass to the subcritical size region and are dissolved.

Thus, the growth process of larger precipitates due to the decrease in the size and disappearance of fine ones plays the determining role. Here, the average size of a precipitate monotonously increases in time. This stage is usually called the Ostwald ripening (OR) of precipitates of a new phase. The alternative term “coalescence” is now used rarely. Grounds of sequential and internally consistent OR theory were laid in the works [11, 12], where it is considered that precipitate growth occurs from the self-consistent average density field of impurity atoms, and one can neglect a direct diffusion interaction of precipitates located close to each other (precipitates are located rather far from each other).

It was shown in the works [6, 8, 11, 12] that kinetics of macrodefects on the OR stage is defined by the tendency to the decrease of the total interfacial surface energy, by the conservation law of a number of impurity atoms which are contained in both the precipitates of a new phase and solid solution, as well as by the mechanism of impurity-atom transfer acting in the system. In a perfect (which does not contain defects) crystalline matrix, the mass transfer velocity is determined either by diffusion through the volume of matrix-crystal [11], or by transition kinetics and atomic structure at the matrix-precipitate interface of a new phase (boundary kinetics) [12]. In a real crystal (which contains different defects), kinetics of macrodefects on the OR stage can be defined by diffusion along dislocation tubes [13-17] or diffusion along interfaces (grain boundaries) of polycrystals [18, 19]. The majority of publications is devoted to the OR of island structures on the solid body surface [20-27]. OR of pores filled by gas [28, 29], OR of multicOMPONENT precipitates of a new phase [8, 21], OR of crystallization centers in kinetics of crystallization of melts [30], and a number of other questions [3, 4, 31-35] were considered as well.

The processes of diffusion decomposition play the important role in material science being one of the reasons of the aging of metal alloys [36-40]. In particular, decomposition of solid solution in modified austenitic stainless steels (structural materials for fast-neutron reactors and future reactors) leads to the formation of G-phase (MnNi12Si5) precipitates and γ-carbides (M6C) that considerably decreases the radiation resistance of steel on further evolution stages of its defect structure [38-40].

In the present work, we theoretically consider the OR of two-dimensional precipitates of a new phase at the grain boundary of finite thickness δ [41-44] taking

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into account the diffusion fluxes of impurity atoms from the grain interior to the grain boundary. As well as in the works [45-51], it is considered that precipitate radius $R$ is small in comparison with the typical length scale of the problem $L_B$ ($R \ll L_B$). It is also considered that precipitate growth is limited by the impurity-atom diffusion in the grain boundary, and not by the surface kinetics of incorporation of impurity atoms into precipitates. Note that OR of three-dimensional precipitates of a new phase at the grain boundary whose shape consists of two spherical segments of the same radius (see Fig. 4.23 in [19]) was theoretically considered earlier in [18, 19]. This work is the natural continuation of the works [49-51] where diffusion growth and morphological stability of the separated (isolated) two-dimensional precipitate of a new phase at the grain boundary were considered. As well as in the works [49-51], for definiteness, we will talk about solid precipitates of a new phase, but formulas obtained later can be also applied for the case of vacancy pores where vacancies play the role of impurity atoms. The last remark concerns the works [49-51], too.

2. BASIC RELATIONS OF THE KINETICS OF OR PRECIPITATES AT THE GRAIN BOUNDARY

As it is shown in the works [49, 50], the diffusion growth velocity of two-dimensional precipitate of a new phase with the base radius $R = R(t)$ and the height $h$ located at the grain boundary has the form

$$\frac{dR}{dt} = \frac{D_B \sigma \delta K_0(R/L_B)}{h L_B F_0(R/L_B)} \Delta n_{BR}$$

(formula (20) in [49]). Here $D_B$ is the coefficient of the grain boundary diffusion, i.e. the volume diffusion coefficient of impurity atoms in the grain boundary (layer thickness is $\delta$; $\sigma$ is the volume per one impurity atom in precipitate; $L_B$ is the typical length scale of the problem (formula (12) in [49]); $K_0(z)$ is the l-order Macdonald function [52],

$$F_0(z) = K_0(z) + \frac{D_B \sigma \delta}{\beta_B L_B} K_1(z),$$

(2)

$\beta_B$ is the surface kinetic coefficient which characterizes the transition rate of impurity atoms from the grain boundary to the precipitate of a new phase; $\Delta n_{BR}$ is the thermodynamically equilibrium drop of the impurity atom density in the grain boundary around precipitate of the radius $R$ (formula (17) in [49]).

Now we will consider only the case of small supersaturations of solid solution of impurity atoms in the grain boundary

$$\Delta_B(t) = \frac{\bar{n}_B(t) - n_{Bc}}{n_{Bc}} \ll 1.$$  

(3)

Here $\bar{n}_B(t)$ is the impurity atom density in the grain boundary far from precipitate of a new phase; $n_{Bc}$ is the thermodynamically equilibrium value of the impurity atom density in the grain boundary near plane surface grain boundary/precipitate of a new phase ($R \to \infty$).

For precipitate of small radius ($R \ll L_B$) in the case of small supersaturations (3) formula (1) takes the form

$$\frac{dR}{dt} = \frac{\Gamma_B D_B \sigma \delta}{h(K_B + D_B/|\beta_B|)} \left( \frac{1}{R^2} - \frac{1}{R}\right)$$

(formula (30) of the work [49]). Here $\Gamma_B = \sigma \delta \sigma / kT$; $\sigma B$ is the specific interfacial energy of the grain boundary/precipitate of a new phase surface; $K$ is the Boltzmann constant; $T$ is the temperature;

$$K_0 = K_0(R/L_B);$$

(5)

$R^*$ is the critical radius of precipitate of a new phase (precipitate with the radius $R > R^*$ increases, and with the radius $R < R^*$ decreases in size). We note that in the case of $R \ll L_B$

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

(6)

where $\gamma = 0.5772...$ is the Euler constant [52], i.e. $K_0$ depends weakly (logarithmically) on the value of $R$.

If growth of small precipitate ($R \ll L_B$) is limited by the impurity-atom diffusion ($Dd\beta_B \to 0$), then from (4) we obtain

$$\frac{dR}{dt} = \frac{\Gamma_B D_B \sigma \delta n_{c0} \delta}{h K_B R} \left( \frac{1}{R^2} - \frac{1}{R}\right) = \frac{D_B \sigma \delta n_{c0} \delta}{h K_B R} \left( \Delta_B - \frac{\Gamma_B}{R}\right);$$

(7)

since in the case of small supersaturations (3) the following formula takes place:

$$\frac{\Gamma_B}{R} = \Delta_B \ll 1$$

(8)

(the first formula of (29) in the work [49]). Introducing the designation

$$D = \frac{D_B \sigma \delta n_{c0} \delta}{h K_B},$$

(9)

expression (7) for the growth rate $dR/dt$ of precipitate we finally write in the form

$$\frac{dR}{dt} = \frac{D}{R} \left( \Delta_B - \frac{\Gamma_B}{R}\right);$$

(10)

We should note that the value of $D$ has dimensionality of diffusion coefficient and is the constant under the condition of neglect of the dependence $K_0$ on $R$ at the specified statement of the problem.

In this work we will consider an ensemble of precipitates of a small size only ($R \ll L_B$), whose growth is limited by the impurity-atom diffusion ($Dd\beta_B \to 0$) in conditions of small supersaturations of solid solution of impurity atoms in the grain boundary ($\Delta_B < 1$). In this case, the growth rate of precipitates has the form of (7) and (10).

Later we will use the following dimensionless values: precipitate radius $\rho = R/R_0; R = R \Delta_B / \Gamma_B$; time $t' = t/\Gamma_B$ where $R_0 = R^* (t')|_{t=0}$ is the initial critical radius of pre-
cipitate, $\Delta_{\text{B0}} = \Delta_B(t)|_{t=0}$ is the initial supersaturation of impurity atoms in the grain boundary, $T_B = R_0^2/4D$ is the typical time of the problem. Then, omitting the stroke at $t$, equation (10) takes the form

$$
\rho^2 \frac{d\rho}{dt} = \rho \frac{x(t)}{x(t) - 1},
$$

(11)

where

$$
x(t) = R^*(t)/R_0^* = \Delta_{\text{B0}}/\Delta_B(t)
$$

(12)

is the dimensionless critical radius of precipitate (the value we are looking for), $x(0) = 1$.

Let $f(\rho, t)$ is the distribution function of precipitates of a new phase by sizes normalized on the precipitate density (a number of precipitates per unit area of the grain boundary), i.e. in such a way that

$$
N(t) = \int_0^\infty f(\rho, t) d\rho
$$

(13)

is the precipitate density; and $f(\rho, t)$ and $N(t)$ should be determined. Distribution function $f(\rho, t)$ satisfies the kinetic equation (continuity equation in the size space) [11, 12]

$$
\frac{\partial f(\rho, t)}{\partial t} + \frac{\partial}{\partial \rho} \left[ f(\rho, t) \frac{\partial \rho}{\partial t} \right] = 0
$$

(14)

with the specified initial distribution function $f_0(\rho) = f(\rho, t)|_{t=0}$ and matter balance equation in the system (the law of conservation of matter)

$$
\pi_{\text{B}0} \delta + \pi_{\text{B}} d + \frac{\pi h}{\omega} R_0^2 \rho^2 f_0(\rho) d\rho = \pi_{\text{B}} (t) \delta + \pi_x (t) d + \frac{\pi h}{\omega} R_0^2 \rho^2 f(t, \rho) d\rho,
$$

(15)

where $\pi_{\text{B}0} = \pi_{\text{B}} |_{t=0}$, $\pi_{\text{B}}$ is the impurity atom density in the grain interior, $\pi_{\text{B}} = n_{\text{B}} |_{t=0}$, $d$ is the typical lateral dimension of the grain.

We note that impurity atoms contained, respectively, in solid solutions of the grain boundary, grain body, and in precipitates of a new phase are taken into account in the law of conservation of matter (15). As well as in the works [49, 50], we will consider that thermodynamic equilibrium between impurity atoms contained in the grain body near grain boundary and impurity atoms in the grain boundary itself exists far from precipitate of a new phase. Then

$$
\pi_{\text{B}} = \pi_{\text{B0}}, \quad \pi_{\text{B}} = \pi_{\text{B0}}
$$

(16)

(formula (10) in [49]). Taking into account correlations (16), we write the law of conservation of matter (15) in the form

$$
Q = \Delta_{\text{B0}} + \kappa^* \int_0^\rho \rho^2 f_0(\rho) d\rho = \Delta_B(t) + \kappa^* \int_0^\rho \rho^2 f(t, \rho) d\rho, (17)
$$

where

$$
k^* = \frac{\pi h R_0^2}{n_{\text{B}} \omega (\delta + C_d)}
$$

(18)

or in the form

$$
\frac{\Delta_{\text{B0}}(t)}{Q} + \kappa^* \int_0^\rho \rho^2 f(t, \rho) d\rho = 1.
$$

(19)

Here

$$
k = \frac{\pi h R_0^2}{n_{\text{B}} \omega (\delta + C_d)}
$$

(20)

is the constant which characterizes the given system. Taking into consideration formula (12), we have

$$
\frac{\Delta_{\text{B0}}}{\Delta_B(t)} + \kappa^* \int_0^\rho \rho^2 f(t, \rho) d\rho = 1.
$$

(21)

Thus, the problem is to discover an asymptotic (at $t \to \infty$) solution of equations (11), (14), and (21) for the specified initial condition $f(\rho, t)|_{t=0} = f_0(\rho)$.

3. ASYMPTOTICS OF CHANGE OF THE PRECIPITATE CRITICAL RADIUS AND SUPERSATURATION OF SOLID SOLUTION OF IMPURITY ATOMS IN THE GRAIN BOUNDARY ON THE OR STAGE

In order to solve the stated problem, firstly, we will find the asymptotic (at $t \to \infty$) of change in the dimensionless precipitate critical radius $x(t) = R^*(t)/R_0^*$ together with the asymptotic of change in the supersaturation of solid solution of impurity atoms in the grain boundary $\Delta_B(t) = \Delta_{\text{B0}}/x(t)$ (see formula (12)).

Based on the works [8, 11], as independent variable in equations (11), (14), and (21), we will choose the relative radius (with respect to the critical one), but not the dimensionless precipitate radius $\rho$

$$
u = \frac{R}{R^*} = \frac{R}{R_0^*} \Delta_B(t) = \frac{\rho}{x(t)}.
$$

(22)

Since supersaturation $\Delta_B(t) \to 0$ at $t \to \infty$, then $x(t) \to \infty$; due to this fact, $x(t)$ can be used for the time reading [8, 11]. As the variable which plays the role of time $t$, it is convenient to choose the value

$$
\tau = \ln x^2 = \ln \left( \frac{R^*(t)}{R_0^*} \right)^2 = \ln \left( \frac{\Delta_{\text{B0}}}{\Delta_B(t)} \right)^2,
$$

(23)

$$
x^2(\tau) = \exp \tau.
$$

(24)

Then, in variables $\nu, \tau$, equation (11) takes the form

$$
\nu \frac{d\nu}{d\tau} = \frac{1}{2} \gamma (\nu - 1) - \nu^2, \quad \nu = \frac{\rho}{x(t)},
$$

(25)

where

$$
\gamma = \gamma(\tau) = \frac{dt}{dx} \frac{3dt}{dx} > 0.
$$

(26)

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Denoting the solution of equation (25) as \(u(\tau, t)\) at the specified initial condition \(u|_{\tau=0} = w\) and taking into account that \(\rho(\tau, t) = x(\rho(\tau, t))\) (see (22)), \(\varepsilon_{\tau, 0} = 0, x(\varepsilon_{\tau, 0}) = 1\), then total number of impurity atoms in precipitates of all sizes per unit area of the grain boundary can be written through the initial distribution function \(f(\rho)\) in the form

\[
N_{i}(t) = \frac{\pi h}{\alpha} \rho^{2} f(\rho, t) d\rho
\]  

(27)

Here \(w(\tau)\) is the solution of equation \(u[w(\tau), \tau] = 0\), i.e. the lower boundary of primary radiuses of precipitates which were not dissolved till time \(\tau\).

Taking into consideration formula (27), we write the law of conservation of matter (21) in the form

\[
\frac{\Lambda w(\tau)}{Q(t)} + \frac{k w(\tau)}{\pi h R_{0}^{2}} N_{i}(\tau) = 1
\]  

(29)

or, finally, taking into account formulas (24) and (28)

\[
1 - \frac{\Lambda w(\tau)}{Q(t)} \exp(-\tau/2) = \kappa(\exp(\tau)) \int_{u(\tau)}^{u(t)} u^{2}(w, t) f(\rho) d\rho
\]  

(30)

\[
\gamma(\tau) = dt/sdx\ dx\text{ is an unknown function in equations (25) and (30) and they should be used in order to define it, i.e. eventually for the determination of the critical radius of precipitate } x(t) \text{ and supersaturation } \Lambda \delta(\tau).
\]

Analysis of equations (25) and (30), which is similar to the analysis performed in the works [8, 11], indicates that at sufficiently large values of time \(\tau\)

\[
\gamma(\tau) = \gamma_{0}[1 - e^{2}(\tau)],
\]  

(31)

where \(\gamma_{0} = \text{const}, \ u(\tau) > 0, \ a(\tau) \to 0 \text{ at } \tau \to \infty\). The value of \(\gamma_{0}\) is defined by the condition of touch by the velocity-time curve \(du/dt = \varepsilon_{2}du/d\tau\) as a function of \(u\) of the abscissa axis

\[
\gamma(u - 1) - \gamma(u) = 0,
\]  

(32)

\[
\frac{\partial}{\partial u}[\gamma(u - 1) - \gamma(u)] = 0
\]  

(33)

(see equation (25)). From equations (32) and (33) we find \(\gamma_{0} = 27/4\), abscissa of the touch point ("locking" point for points moving from the right to the left along the \(u\)-axis) \(u_{0} = 3/2\). As seen from formula (31), points approaching from the right to \(u_{0}\) pass slower through the "locking" point \(u_{0} = 3/2\). The velocity of this passage is determined by the value of \(\alpha(\tau)\), which, as well as the value of \(\gamma(\tau)\), should be obtained from equation (30) and equation of motion (25)

\[
u \frac{du}{dt} = -\frac{1}{2} \left( u - \frac{3}{2} \right) (u + 3) - \frac{27}{8} \varepsilon^{2}(\tau)(u - 1).
\]  

(34)

In the vicinity of the point \(u_{0} = 3/2\), i.e. at \(|u - u_{0}| \leq \delta(\tau)\) the rate \(du/d\tau\) is the following:

\[
\frac{du}{dt} = -\left( u - \frac{3}{2} \right)^{2} - \frac{3}{4} \varepsilon^{2}(\tau).
\]  

(35)

Introducing new variable \(z = (u - 3/2)/\varepsilon\) as ratio of two small values, we write equation (35) as follows

\[
\frac{1}{\varepsilon} \frac{dz}{dt} = -z^{2} - \frac{3}{4} \frac{d(1/\varepsilon)}{d\tau} > 0.
\]  

(36)

Let us designate

\[
\alpha = \alpha(\tau) = \frac{d(1/\varepsilon)}{d\tau} = \frac{1}{\varepsilon^{2}} > 0.
\]  

(37)

Then equation (36) takes the form

\[
\frac{1}{\varepsilon} \frac{dz}{dt} = -z^{2} - \frac{3}{4} \alpha = 0.
\]  

(39)

Similarly to the behavior of \(\gamma = \gamma(\tau)\), asymptotically (at \(\tau \to \infty\)) \(\alpha(\tau) \to \alpha_{0}\), where \(\alpha_{0} = \text{const}\). As well as in the case of the determination of the value of \(\gamma_{0}\), \(\alpha_{0}\) is defined by the condition of touch by the velocity-time curve \(dz/d\tau\) as a function of \(z\) of the abscissa axis

\[
-z^{2} - \frac{3}{4} \alpha z = 0,
\]  

(39)

\[
\frac{d(1/\varepsilon)}{d\tau} \to 3/2, \ \varepsilon(\tau) \to \frac{1}{3\tau^{2}}.
\]  

(40)

From equations (39), (40) we find \(\alpha_{0} = 3^{1/2}\), abscissa of the touch point ("locking" point for points moving from the right to the left along the \(z\)-axis) \(z_{0} = 3^{3/2}/2\). Then, asymptotically (at \(\tau \to \infty\))

\[
\frac{d(1/\varepsilon)}{d\tau} \to 3/2, \ \varepsilon(\tau) \to \frac{1}{3\tau^{2}}.
\]  

(41)

In this case

\[
3/2 \frac{dz}{d(\ln \tau)} \to \frac{\left( z - \frac{3}{2}\right)^{2}}{2},
\]  

(42)

i.e. velocity \(dz/d(\ln \tau)\) asymptotically tends to zero in the "locking" point \(z_{0} = 3^{3/2}/2\).

Thus, at sufficiently large \(\tau\) corrected value of \(\gamma(\tau)\) will be the following:

\[
\gamma(\tau) = \gamma_{0}[1 - \frac{1}{3\tau^{2}}],
\]  

(43)

and corrected position of "locking" point on the \(u\)-axis

\[
u_{0}(\tau) = 3/2 + z_{0}(\tau) \to 3/2 + 1/2 \tau.
\]  

(44)

From equations (26) and (43) we obtain

\[
\frac{3\delta}{dx^{3}} = \gamma(\tau) = \gamma_{0}[1 - \frac{1}{3\tau^{2}}],
\]  

(45)

where \(\tau = \ln x^{2}\) (formula (23)) and, correspondingly,

\[
x(\tau) = \frac{4}{9} \left( 1 + \frac{3}{4(\ln \tau)^{2}} \right).
\]  

(46)

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Returning to the dimensional variables (critical radius of precipitate \( R(t) \) and time \( t \)), from formula (46) we find

\[
R^3 = \frac{4}{9} \Gamma g D t \left[ 1 + \frac{3}{4} \left( \ln \left( \Gamma g D t / R^3 \right) \right)^2 \right].
\] (47)

It is seen from formulas (45) and (47) that basic approximation \( j(r) \equiv j_0 \) and, correspondingly, formula

\[
R^3 = \frac{4}{9} \Gamma g D t \frac{4 \Gamma g D n_p \exp \delta}{h k_0}
\] (48)

are true under the condition \( 1/3 \delta^2 << 1 \), i.e.

\[
\left[ \ln \left( \Gamma g D t / R^3 \right) \right]^2 >> 1.
\] (49)

Supersaturation of solid solution of impurity atoms in the grain boundary asymptotically (at \( t \to \infty \)) is the following:

\[
\Delta_g(t) = \left( \frac{3}{2} \right)^{2/3} \left[ \frac{\Gamma g h k_0}{D g n_p \exp \delta} \right]^{1/3} t^{-1/3}.
\] (50)

We note that explicit dependence \( \tau = \tau(t) \) appears from formulas (23) i (48)

\[
\tau(t) = 2 \ln \left[ \left( \frac{2}{3} \right)^{2/3} \left( \frac{\Gamma g D n_p \exp \delta}{h k_0} \right) t ^{1/3} \frac{1}{R_0^3} \right].
\] (51)

Outside the “locking” point \( u_0 = 3/2 \) in equation (25) one can state \( \gamma = \gamma_0 = 27/4 \) and then

\[
\frac{d u}{d \tau} = V(u),
\] (52)

where

\[
V(u) = -\left( u - \frac{3}{2} \right)^2 u + \frac{3}{2} u^3.
\] (53)

4. ASYMPTOTICS OF THE DISTRIBUTION FUNCTION OF PRECIPITATES OF A NEW PHASE AND PRECIPITATE DENSITY ON THE OR STAGE

We will search the distribution function of precipitates of a new phase by sizes in variables \( u, \tau \). In these variables distribution function \( \phi(u, \tau) \) is connected with function \( f(p, t) \) by the correlation

\[
\phi(u, \tau) \, du = f(p, \tau) \, dp = x \phi(p, \tau) \, du,
\] (54)

whence it follows that

\[
f = \frac{\phi(u, \tau)}{x(\tau)}. \tag{55}
\]

Kinetic equation for the distribution function \( \phi(u, \tau) \) outside the point \( u_0 = 3/2 \) at \( \tau \to \infty \) takes the form

\[
\frac{\partial \phi(u, \tau)}{\partial \tau} + \frac{\partial}{\partial u} \left( \phi(u, \tau) \frac{df}{du} \right) = 0, \tag{56}
\]

where function \( V(u) \) is represented by formula (53).

Asymptotics of the distribution function \( \phi(u, \tau) \) (at \( \tau \to \infty \)) are the following

\[
\phi(u, \tau) = \begin{cases} \frac{\phi(\tau - \tau(u))}{-V(u)}, & u < u_0, \\ 0, & u \geq u_0, \end{cases} \tag{57}
\]

where \( \tau(u) = \frac{u}{V(u)} \),

\[
\tau(u) = -\frac{8}{9} \ln(u + 3) - \frac{10}{9} \ln \left( \frac{3}{2} - u \right) \left( \frac{3}{2} - u \right)^{-1} + B, \tag{58}
\]

\[
B = 2 \ln(3e^{3/2}2^{3/2}), \quad \pi(0) = 0, \quad \pi(u - 0) \to \pi, \quad u \to 0, \to \infty, \text{ and } \phi \text{ is an arbitrary differentiable function which should be determined.}
\]

Distribution function on the right from the point \( u_0 \) at \( \tau \to \infty \) is determined by points which come here from the infinitely distant region and such that correspond to precipitates on a “tail” of their initial (at \( \tau = 0 \)) distribution. Since a number of precipitates in this distribution rapidly (in fact, exponentially) decays with the growth of their sizes, then distribution function in the range of \( u > u_0 \) (outside the vicinity of the point \( u_0 \)) tends to zero at \( \tau \to \infty \).

To determine the function \( \phi \), we will use the low of conservation of matter (30) which we write in the form

\[
1 - \frac{\Delta_{R_0}}{Q} \exp(-\tau/2) = \kappa(\exp \tau) \phi(u, \tau) \, du. \tag{59}
\]

Since at \( \tau \to \infty \) \( \exp(-\tau/2) \to 0 \) and function \( \phi(u, \tau) \) has the form of (57), we obtain the following asymptotic equation for \( \phi \)

\[
1 = \kappa(\exp \tau) \phi(\tau - \tau(u)) \left[ \frac{u^2}{-V(u)} \right] \, du. \tag{60}
\]

Expression in the right side of equality (60) can be independent of \( \tau \) only if function \( \phi \) has the form

\[
\phi(\tau - \tau(u)) = A \exp(-\tau + \tau(u)). \tag{61}
\]

Then, at \( u < u_0 \) \( \phi(u, \tau) = -A \left[ V(u) \right]^{-\tau} \exp(-\tau + \tau(u)) \),

\[
\phi(u, \tau) = A \exp(-\tau) \left[ \frac{3e^{3/2}2^{3/2}}{2^{3/2}u + 3} \right]^{-\tau} \exp\left( -\frac{3}{2} - u \right). \tag{62}
\]

Hence, it is seen that asymptotic (at \( \tau \to \infty \)) behavior of the distribution function of precipitates of a new phase by sizes does not depend on the form of the initial distribution function.

We write function \( \phi(u, \tau) \) for the whole range of \( u \) variation \( 0 \leq u < \infty \) as follows

\[
\phi(u, \tau) = A \exp(\tau) P(u), \tag{63}
\]

where \( P(u) = -\exp(\tau(u))/V(u) \), \( u < u_0 \).
According to (13), (63), and (66), density of precipitates of a new phase will be equal to
\[ N = \frac{1}{4} \int_{0}^{\infty} f(\rho, \tau) d\rho = \frac{1}{4} \varphi(u, \tau) du = A \exp(-\tau) . \] (73)

Then, as it follows from formulas (63) and (73)
\[ \varphi(u, \tau) = N(\tau) P(u) . \] (74)

Taking into account formulas (23) and (48), from (73) we obtain
\[ N(t) = A \left( \frac{R_0}{R(t)} \right)^2 = \left( \frac{3}{2} \right)^{4/3} A R_0^2 \left( \frac{\Gamma_d A_{n_\rho_\rho} \omega_0^2}{\pi h_0^2} \right)^{-2/3}. \] (75)

In expression (75), as it appears from (20), (67), and
\[ A R_0^{-2} = \frac{R_0^{-2}}{\kappa u^2} = \frac{n_{\rho_\rho} Q_0 (\delta + C \delta)}{\pi h_0^2}, \] (76)
i.e. asymptotically (at \( t \to \infty \)) \( N(t) \) does not depend on the value of \( R_0 \).

Since \( \bar{\rho} = \bar{R}/R' \), the average radius of precipitate asymptotically increases with time proportional to the critical radius
\[ \bar{R}(t) = \frac{\pi R'(t)}{4}, \] (77)
where
\[ \bar{\rho} = \frac{1}{u_0} \int_{0}^{u_0} u P(u) du = 1.0665 . \] (78)

In order to write the asymptotic expression of the distribution function of precipitates by sizes in variables \( R, t \), we firstly note
\[ f(R, t) dR = \varphi(u, \tau) du = \varphi(u, \tau) \frac{dR}{R^2}, \] (79)
\[ f(\bar{R}, t) = \varphi(u, \tau) \frac{d\bar{R}}{R(t)} . \] (80)

5. ASYMPTOTICS OF THE FACTOR OF GRAIN BOUNDARY FILLING WITH PRECIPITATES OF A NEW PHASE ON THE OR STAGE AND LIMITS OF VALIDITY OF THE PERFORMED INVESTIGATION

By analogy with publications [23-25], we introduce the factor of grain boundary filling with precipitates of a new phase \( Z(t) \) as the area which is covered by precipitates on the unit area of the grain boundary
\[ Z(t) = \pi R_0^2 \int_{0}^{\infty} f(R, t) dR = \pi R_0^2 \int_{0}^{\infty} f(\bar{R}, t) d\bar{R} . \] (81)

Taking into account correlations (68), (74), and (79), we write formula (81) at \( t \to \infty \) in the form

According to (13), (63), and (66), density of precipitates of a new phase will be equal to
We consider that this condition is fulfilled at

\[
12 \left( \ln \frac{R'(t)}{R'_0} \right)^{1/2} \geq 10, \quad \ln \frac{R'(t)}{R'_0} \geq \left( \frac{5}{6} \right)^{1/2},
\]

i.e. at \( R'(t)/R'_0 \geq 2.4915, \ R(t)/R'_0 \geq 2.6572 \) \( \bar{R}(t), \ R'(t) \) are connected by formulas (77) and (78). We note that choice of the initial moment of time \( t = 0 \) is determined by the diffusion relaxation of \( \bar{R} \) to \( R'(t) \) \( (\bar{R}(0) \sim R'(0)) \) in the obtained inequalities.

We should also note that consideration of the problem performed in the approximation of self-consistent average field \[8, 11\], when diffusion fields of separate precipitates almost do not overlap, and we can neglect their direct diffusion interaction (the average distance between precipitates is \( \Lambda \gg R \ln(L_B/R) \)).

6. CONCLUSIONS

Thus, we have theoretically considered the OR process of two-dimensional (plane) small-size precipitates \((R << L_0)\) of a new phase located in the grain boundary of finite thickness \( \delta \) taking into account diffusion fluxes of impurity atoms from the grain interior of typical size \( d \) \( (d \gg R, d \gg \delta) \) to the grain boundary. It is assumed that growth of precipitates is limited by the impurity-atom diffusion \((D_B \beta_0 \ll R\bar{K}_0(L/L_0))\) in the grain boundary; in this case, growth rate of separate precipitate takes form of (7), (10). As well as in the works \[8, 11\], it is considered that precipitate growth occurs from self-consistent average field of impurity atoms, and direct diffusion interaction of precipitates on short distances from each other can be neglected.

Asymptotic \((t \to \infty)\) time dependences of the precipitate critical radius \( R'(t) \) \( ((46)-(48)) \), supersaturation of solid solution of impurity atoms in the grain boundary \( \Delta_B(t) \) \( ((50)) \), precipitate density \( N(t) \) \( ((75), (76)) \), distribution function of precipitates by sizes \( f(R, t) \) \( ((64)-(65), (80)) \), factor of grain boundary filling with precipitates \( Z \) \( ((83)) \), total number of impurity atoms in precipitates per unit area of the grain boundary \( N \) \( ((88)) \) are obtained. It is shown that asymptotically average radius of precipitate increases proportionally to the critical radius \( \bar{R}(1) = 1.0665 \times R'(t) \) \( ((77) \text{ and } (78)) \), and asymptotic behavior of the distribution function of precipitates of a new phase by sizes does not depend on the form of the initial distribution function.

Limits of application of the performed investigation are discussed (see inequalities (89) and (90) and the corresponding narration in Section 5).

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