A new kinetic model for precipitation from solid solutions

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This paper introduces a new kinetic model for homogeneous precipitation from solid solutions. By considering the elementary acts of migration of point defects (interstitials and/or vacancies) across a precipitate-matrix interface, one is able to derive equations for the rates of emission and absorption of solute atoms at the interface. These latter are different from those used in the classical nucleation rate theory, but asymptotically give the Lifshitz-Slyozov-Wagner coarsening regime (Ostwald ripening) for precipitation from supersaturated solid solutions. The model allows to derive a total solubility limit as a function of two dimensionless model parameters. A contribution from heterophase fluctuations (subcritical precipitates) to the total solubility limit, depending on the values of the model parameters, may exceed by several orders of magnitude the solubility of single atoms.
The results obtained allow for a qualitative explanation of the anomalous total oxygen solubility of about 1000 ppm recently observed in several oxide dispersion strengthened ferritic steels, the single atomic oxygen solubility in the bcc iron matrix being only about 1 ppm.

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The quantitative studies of the kinetics of precipitation from solid solutions originate from the pioneering work by Ostwald [1]. The late stage of this process, called coalescence, is governed by the theory elaborated by Lifshitz, Slyozov [2] and Wagner [3]. Along with this, a general theory of precipitation is mainly based on the classical nucleation-growth model, including its modifications and extensions, which is still debated in some of its aspects (see e.g. [4] and references therein). In particular, one of the open questions is a method of determination of the rates of emission and absorption in the master equation [4]. The present work proposes a solution for this problem.

This Letter introduces a new phenomenological kinetic model, being an extension of the recently published model of homogeneous semicoherent interphase boundary [4], based on consideration of the kinetics of point defects (PDs) at a precipitate-matrix interface. It is well known that diffusion in solids is possible only due to the presence of PDs. This paper shows that PDs play the same crucial role for precipitation in solids.

Consider an interphase boundary (Gibbs interface) between a precipitate, consisting of atoms of several types, labeled \( j = 1, ..., n \), and a solution of these atoms in a solid matrix. Let the interface between the precipitate and the matrix be coherent, i.e. most of the atomic planes be continuous across it. Since the bulk physical properties of such heterophase structure are discontinuous across the interface, the number density (concentration) profiles of PDs are expected to be discontinuous as well. The PDs can penetrate across the interface via the thermal activation or some other mechanism. Therefore, the transfer of PDs across the interface can be considered as a reversible surface chemical reaction.

An interstitial atom of the type \( j \) (\( j \)-atom), located at one side of the interface, can transfer to the other side of the interface and vice versa. This process can be represented in the form of a reversible chemical reaction:

\[
\hat{i}_j^p \rightleftharpoons \hat{i}_j^m .
\]

where \( \hat{i}_j^p \) denotes an interstitial \( j \)-atom in the precipitate \((\varphi = p)\) or in the matrix \((\varphi = m)\). In this case, the rate of transitions, represented by Eq. (1), in each direction, is proportional to a concentration \( c_j^p \) of the interstitials \( \hat{i}_j^p \) in the corresponding phase and the normal component of the flux of interstitial \( j \)-atoms across the interface is as follows (hereinafter the normal unit vector is supposed to be directed from the precipitate into the matrix):

\[
\dot{j}_{ij} = \beta_{ij}^p c_j^p - \beta_{ij}^m c_j^m ,
\]

\( \beta_{ij}^p \) being a phenomenological transition kinetic coefficient for interstitials in the corresponding phase.

A \( j \)-atom, located at a regular lattice site at one side of the interface, can transfer to a neighboring vacant site at the other side of the interface and vice versa. This process can be represented in the form of a reversible chemical reaction:

\[
l_j^m + v_j^p \rightleftharpoons l_j^p + v_j^m ,
\]

where \( l_j^m \) is a \( j \)-atom at a regular lattice site of the matrix; \( v_j^p \) is a vacant regular lattice site in the \( j \)-th sublattice of the precipitate; \( l_j^p \) is a \( j \)-atom at a regular site of the \( j \)-th sublattice of the precipitate; \( v_j^m \) is a vacant regular lattice site in the matrix. Therefore, the rate of transitions, represented by Eq. (2), in each direction, should be bilinear in concentrations of the corresponding reagents and the normal component of the flux of vacancies across the interface via the regular lattice sites occupied by \( j \)-atoms is as follows:

\[
\dot{j}_{ij} = \beta_{ij}^p c_{ij}^p c_j^m - \beta_{ij}^m c_{ij}^m c_j^p .
\]

Here \( c_{ij}^p \) is a concentration of vacancies, which belong to the \( j \)-th sublattice of the precipitate, \( c_{ij}^m \) is a concentration of \( j \)-atoms at the regular lattice sites of the matrix,
is a concentration of vacancies in the matrix, \( c_j^v \) is a concentration of \( j \)-atoms, which belong to the regular lattice sites of the precipitate and \( \beta_j^v \) is a phenomenological transition kinetic coefficient for vacancies in the corresponding phase.

An interstitial atom located at one side of the interface can recombine with a vacancy located at the other side:

\[
\begin{align*}
  j_j^p + v^m & \rightarrow I_j^m, \\
  j_j^m + v_j^p & \rightarrow I_j^p.
\end{align*}
\]

These are irreversible reactions, since an energy threshold for production of the Frenkel pairs is usually large. The normal component of the flux of \( j \)-atoms via the recombination mechanism (9) is as follows:

\[
  j_{R_j} = \alpha_{R_j}^c c_j^p c_j^v - \alpha_{R_j}^m c_j^m c_j^p, \tag{6}
\]

where \( \alpha_{R_j}^c \) is a phenomenological recombination kinetic coefficient in the corresponding phase.

Suppose, that the flux of \( j \)-atoms across the interface is related to the partial fluxes of PDs, given by Eqs. (2), (4) and (6), in the next usual way:

\[
  j_j = j_{i_j} - j_{v_j} + j_{R_j} \tag{7}
\]

A total concentration of \( j \)-atoms in the corresponding phase consists from the concentrations of the atoms in both the interstitial and regular positions: \( c_j^i = c_j^i + c_j^v \). One can consider the next relations between the concentrations of \( j \)-atoms in different lattice positions:

\[
  c_j^i = x_j^i c_j^i; \quad c_j^v = (1 - x_j^i) c_j^v, \tag{8}
\]

where \( x_j^i \) is a dimensionless constant, taking its value from the range \( 0 \leq x_j^i \leq 1 \). The lower and upper limiting values correspond to the cases, when the solute atoms reside only in the regular and interstitial lattice positions, respectively. Then, taking into account Eqs. (4), (9) and (8), one can represent Eq. (2) as follows:

\[
  j_j = c_j^p \left[ \beta_j^p x_j^p + \beta_j^m x_j^m (1 - x_j^p) + \alpha_{R_j}^p x_j^p c_j^v \right] - c_j^m \left[ \beta_j^m x_j^m + \beta_j^v c_j^v (1 - x_j^m) + \alpha_{R_j}^m x_j^m c_j^v \right]. \tag{9}
\]

A state of kinetic equilibrium at the interface is determined by the condition that the solute flux across it turns to zero:

\[
  j_j^{eq} = 0. \tag{10}
\]

Taking into account Eq. (9), one can find from Eq. (10) a relation between the equilibrium solute and PDs concentrations at the interface:

\[
  \begin{align*}
    c_j^{eq} = & \frac{\beta_j^p x_j^{eq} + \beta_j^m (1 - x_j^{eq}) + \alpha_{R_j}^p x_j^{eq} c_j^{eq}}{\beta_j^m x_j^{eq} + \beta_j^v (1 - x_j^{eq}) + \alpha_{R_j}^m x_j^{eq} c_j^{eq}} c_j^{eq}, \\
    c_j^{eq} = & \frac{\beta_j^p x_j^{eq} + \beta_j^m (1 - x_j^{eq}) + \alpha_{R_j}^p x_j^{eq} c_j^{eq}}{\beta_j^m x_j^{eq} + \beta_j^v (1 - x_j^{eq}) + \alpha_{R_j}^m x_j^{eq} c_j^{eq}} c_j^{eq}. \tag{11}
  \end{align*}
\]

In the absence of external perturbations, which violate a conservativity of the system (e.g. irradiation, which produces nonequilibrium PDs), the conditions of kinetic and thermodynamic equilibrium should be equivalent. Therefore, Eq. (11) is equivalent to the Gibbs-Thomson relation for the equilibrium solute concentration near the interface:

\[
  c_j^{eq} (r_p) = c_j^{eq} \exp (a/r_p), \tag{12}
\]

where \( c_j^{eq} \) is a thermodynamic equilibrium solubility, \( r_p \) is a radius of the precipitate, \( a = 2 \gamma \omega_0 / k_B T \), \( \gamma \) is a coefficient of surface tension at the interface, \( \omega_0 \) is a mean atomic volume, \( k_B \) is the Boltzmann’s constant and \( T \) is temperature.

Now we consider a problem of solute diffusion in the matrix near a spherical precipitate of a radius \( r_p \). A steady-state solute concentration profile in the matrix is subject to the next diffusion equation:

\[
  \text{div} j_j^m = 0; \quad j_j^m = -D_j^m \nabla c_j^m, \tag{13}
\]

where \( D_j^m \) is a solute diffusion coefficient in the matrix.

The normal component of the solute flux across the interface is given by Eq. (9). In the first order in a deviation of the solute concentration at the interface from its kinetic equilibrium value (11), Eq. (9) becomes

\[
  j_j^{eq} (r_p) = D_j^m \left[ c_j^{eq} (r_p) - c_j^{eq} (r_p) \right] / l, \tag{14}
\]

where

\[
  l = D_j^m / \left\{ \beta_j^{eq} x_j^{eq} + \beta_j^v (1 - x_j^{eq}) + \alpha_{R_j} x_j^{eq} c_j^{eq} \right\}, \tag{15}
\]

is a model parameter with a dimension of length.

One can consider the second boundary condition as follows:

\[
  c_j^{eq} (\infty) = \bar{c}_j^m, \tag{16}
\]

where \( \bar{c}_j^m \) is an average concentration of the solute monomers in the matrix.

A solution of the diffusion equation (13) with the boundary conditions, given by Eqs. (14) and (16), gives:

\[
  c_j^{eq} (r_p) = \bar{c}_j^m + r_p \left[ c_j^{eq} (r_p) - \bar{c}_j^m \right] / (r_p + l). \tag{17}
\]

From Eq. (17) one can see that in a general case of a finite value of \( l \), the steady-state value of the solute concentration at the interface is different from the equilibrium one and saturates to it for \( r_p \gg l \). This is a specific feature of the model, originating from the boundary condition Eq. (14).

A total number \( N \) of atoms entering the precipitate is a sum of the numbers \( N_j \) of \( j \)-atoms: \( N = \sum_{j=1}^{n} N_j \). The number \( N_j \) is subject to the next kinetic equation:

\[
  dN_j / dt = -4 \pi r_p^2 j_j (r_p). \tag{18}
\]
Taking into account that $N_j = c_j^s \omega_0 N$ and assuming that the chemical composition (stoichiometry) of the precipitate is conserved: $c_j^s = \text{const}_j$, one can derive from Eqs. (13) and (14) a kinetic equation for the total number of atoms in the precipitate:

$$dN/dt = -4\pi r_p^2 D_j^m [c_j^m (r_p) - c_j^m (r_p)] / lc_j^p \omega_0. \quad (19)$$

Below we study the case of homogeneous precipitation from a solid solution in the framework of the Becker-Döring approach [6]. In further considerations it is convenient to change to a dimensionless time variable

$$\tau = t \cdot 4\pi r_0^2 D_j^m \epsilon_j^m \exp / lc_j^p \omega_0, \quad (20)$$

where $r_0 = \sqrt[3]{3\omega_0/4\pi}$.

A distribution function $g(N, \tau)$ of the precipitates is subject to the next kinetic (master) equation [8], valid for $N > 1$:

$$\partial g(N, \tau) / \partial \tau = J_{N-1,N} - J_{N,N+1}; \quad (21)$$

$$J_{N-1,N} = w_e (N - 1) g(N - 1, \tau) - w_a (N) g(N, \tau), \quad (22)$$

where $w_e (N)$ and $w_a (N)$ are respectively the rates of emission and absorption of solute monomers at the precipitate-matrix interface.

As a boundary condition, the next expression is applied: $g(N_{\text{max}}, \tau) = 0$ [7]. The system of Eqs. (21) must be supplemented with an additional equation for the value

$$g(1, \tau) \equiv \tilde{c}_j^m (\tau) / \epsilon_j^m \exp, \quad (23)$$

to satisfy the law of conservation of the total number of solute atoms:

$$\partial g(1, \tau) / \partial \tau = - \sum_{N=2}^{N_{\text{max}}} N \partial g(N, \tau) / \partial \tau. \quad (24)$$

From Eq. (19), taking into account Eqs. (12), (17) and time renormalization (20), one finds [8]:

$$w_e = \sqrt{\lambda N^2} \exp \left( a/r_0 \sqrt{N} \right); \quad (25)$$

$$w_a = \sqrt{\lambda N^2} \exp \left( a/r_0 \sqrt{N} \right) \times \left\{ 1 + \left[ g(1, \tau) \exp \left( -a/r_0 \sqrt{N} \right) - 1 \right] l / (l + r_0 \sqrt{N}) \right\}. \quad (26)$$

Under the condition of detailed balance, when the flux of precipitates in the dimension space (22) turns to zero for any $N$:

$$J_{N-1,N} = 0, \quad \forall N \quad (27)$$

[FIG. 1. A total solubility limit $q^*$ vs. model parameters $a \equiv a/r_0$ and $\lambda \equiv l/r_0$.]

Provided that $\lim_{N \to \infty} g_0(N) = 0$, the condition (27) may be satisfied in the range $0 \leq g_0(1) \leq 1$, which corresponds to the case of a solid solution undersaturated in monomers (see Eq. (23)).

A total concentration of solute atoms in the matrix (expressed in the units of $\epsilon_j^m \exp$) can be calculated as follows:

$$q = \sum_{N=1}^{N_{\text{max}}} N g(N). \quad (29)$$

In the limiting case $g_0^* (1) = 1$, corresponding to the saturated solution of monomers, Eq. (29) with $g(N) = g_0^* (N)$ can be utilized to calculate a total solubility limit, taking into account both the solute monomers and heterophase fluctuations (subcritical precipitates).

Fig. 1 shows the total solubility limit $q^*$ as a function of two dimensionless model parameters $a \equiv a/r_0$ and $\lambda \equiv l/r_0$, entering Eqs. (26) and (27). From Fig. 1 one can see that, within the present model, a contribution from the subcritical precipitates to the total solubility limit, depending on the values of the model parameters, may exceed by several orders of magnitude the solubility of monomers.

To illustrate the precipitation kinetics, resulting from the present model, below we perform calculations for the next two sets of the model parameters: i) $\alpha = 1$; $\lambda = 0.1$; $q^* = 10600$, corresponding to a "strong" precipitation regime ($q^* \gg 1$) and ii) $\alpha = 3.089$; $\lambda = 4.58$; $q^* = 1.931$, corresponding to a "weak" precipitation regime ($q^* \geq 1$). Fig. 2 shows a solution of the system of Eqs. (21), (22) at $\tau = 10^{10}$ in the strong and weak precipitation regimes, with $g(1, \tau = 0) = 0.9q^*(\alpha, \lambda)$ as an
give 10% less than the total solubility limit. Our calculations indicated, together with a stationary distribution function of Eqs. (21), (24) at $g(N_\infty=10^9)$ calculated distribution functions asymptotically tend to the precipitation regimes, with $g_\alpha(N)$ as a critical precipitate size, for which Eq. (19) turns to zero for $N_\lambda$. One can see that, while the LS distribution turns to zero for $N_\lambda=27/8 \cdot N_\kappa$, where $N_\kappa = (\alpha/\ln g(1, \tau))^3$ is a critical precipitate size, for which Eq. (19) turns to zero, the calculated distribution has a nonzero tail in this region.

This behavior is qualitatively similar to that of the oxide precipitates, recently observed in some oxide dispersion strengthened ferritic steels with a total oxygen concentration of about 1000 ppm [9, 10]. Namely, at temperatures below 1150°C the oxide nanoprecipitates are stable with respect to coarsening, while above 1200°C they exhibit Ostwald ripening. In the framework of the present model one can speculate that the total solubility limit of oxygen in these steels approaches 1000 ppm in this narrow temperature range and, since the dependence of the total solubility limit on $\lambda$ is very strong (see Fig. 1), even minor temperature variation of $\lambda$ can push the system onto a different side of the surface depicted in Fig. 1 It is worth noting that, since the solubility limit of single oxygen atoms in the bcc iron matrix is only about 1 ppm [11], the major amount of oxygen in these materials is confined to the oxide nanoprecipitates. Therefore, using the terminology introduced above, oxygen can be classified as a "strong" precipitator in this case.

In summary, the present model, based on consideration of the elementary acts of migration of point defects across a precipitate-matrix interface in a solid solution, allows for a direct derivation of the rates of emission and absorption of solute atoms at the interface and, therefore, gives a possibility to study the kinetics of homogeneous precipitation from solid solutions. Given expressions for interatomic potentials in a real alloy, the model parameters $\lambda$ and $\alpha$ could be calculated by the methods of molecular dynamics simulations. The results obtained apply to the kinetics of precipitation in any other system, where the boundary condition of the type of Eq. (14) is applicable.

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initial condition, corresponding to the state of a homogeneous solid solution with a total solute concentration 10% less than the total solubility limit. Our calculations give $g(1, \tau = 10^{10}) = 0.997$ and 0.914 in the strong and weak precipitation regimes, respectively, and the calculated distribution functions asymptotically tend to the stationary ones. Fig. 3 shows a solution of the system of Eqs. (21), (24) at $g(N_\lambda=10^9)$ in the strong and weak precipitation regimes, with $g(1, \tau = 0) = 1.9g^* (\alpha, \lambda)$ as an initial condition, corresponding to the state of a homogeneous solid solution with a total solute concentration exceeding the total solubility limit by 90%. Our calculations give $g(1, \tau = 10^{10}) = 1.002$ and 1.001 in the strong and weak precipitation regimes, respectively, and the tails of the calculated distribution functions can be approximated by the Lifshitz-Slyozov (LS) distribution [2]. One can see that, while the LS distribution turns to zero for $N \geq 27/8 \cdot N_\kappa$, where $N_\kappa = (\alpha/\ln g(1, \tau))^3$ is a critical precipitate size, for which Eq. (19) turns to zero, the calculated distribution has a nonzero tail in this region.

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