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Modelling of dissolution profiles of ordered particles under irradiation

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Abstract

The interpretation of experiments on the stability of ordered precipitates in irradiation environments demands the detailed knowledge of the 3-d concentration profiles during the dissolution under the irradiation. They can be calculated by a numerical solution of the appropriate time-differential Ginzburg–Landau (TDGL) equations in adiabatic approximation. The profiles are used for the discussion of the experimentally investigated interdependence of dissolution and disordering of the ordered precipitates under irradiation by field-ion microscopy with atom probe (FIM-AP) and by transmission electron microscopy (TEM). Theoretical correlation coefficients are calculated for various composition profiles. By comparison with the correlation coefficients determined from the experimental FIM-AP data, the dissolution process could be identified. At low temperatures, the ballistic mixing is dominant and the precipitate dissolves by a normal diffusion process. At higher temperatures, the profiles have a non-Gaussian shape during dissolution. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The properties of many technical alloys depend on stability of ordered precipitates in materials. For the application of such alloys to fusion reactors, their behaviour has been investigated theoretically and experimentally in great detail (see Ref. [1] for an extensive review of relevant publications until 1984). Recently, theoretical treatments of the coupled change of the local degree of order and of the composition have been developed [2–5] and have been applied to the evolution of the degree of order inside the precipitate and the composition profile around the precipitate as a function of irradiation parameter and temperature. Experimentally, the combined determination of the degree of order and of the composition of irradiated γ' precipitates in Nimonic PE16 was performed by two techniques [6,7]. Field-ion microscopy with atom probe (FIM-AP) is adequate to resolve the compositional dissolution and transmission electron microscopy (TEM) can be used to determine the average degree of order. A correlation analysis of the FIM-AP concentration depth profiles can be used to follow the dissolution of the γ' particles with irradiation time. The time dependent experimental correlation coefficients give a measure of the progress of the dissolution and can be compared with theoretical coefficients. This causes no problem of interpretation at low temperatures when the precipitates first disorder and then dissolve with a Gaussian composition profile for which the theoretical correlation coefficients are known [8,9]. For higher temperatures, however, when the precipitates dissolve in an ordered state, the composition profile shows a discontinuity at the order–disorder transition. The precipitate shrinks, keeping a significant volume fraction of material in the ordered state. For a discussion of the experimental data in this temperature interval non-Gaussian composition profiles have to be used in order to calculate the corresponding correlation coefficients.

In this paper, the time-differential Ginzburg–Landau (TDGL) equations are used for the determination of the composition profiles. However, in order to facilitate the calculation, an adiabatic elimination of the fast changing variable, i.e. the degree of order, is applied leading to

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a single diffusion equation for the composition with an effective, composition dependent diffusion coefficient. This approximation is checked for the 1-d case by the comparison with the exact solution of the TDGL equation. From 3-d composition profiles, the theoretical correlation coefficients are obtained and used for the discussion of the experimentally measured correlation coefficients in the high temperature regime of the dissolution of the ordered precipitate under irradiation [8,9].

2. Composition profiles in adiabatic approximation

In the preceding publications [2–5] 1-d or 2-d profiles of the concentration and of the state of order were obtained. However, for application to the experimental FIM-AP data, 3-d composition profiles are needed in order to calculate the corresponding correlation coefficients which have to be compared with the experimentally determined ones. The 3-d profiles can be obtained by solving the coupled TDGL equations given in Refs. [4,5] as in the 1-d and 2-d case, which needs an elaborate numerical treatment. Instead of doing this, an adiabatic elimination of the fast changing variable, i.e. the degree of order, is applicable. It reduces the problem to the solution of a single partial differential equation for the evolution of the composition.

In the TDGL approach of a tri-critical system [10], the time evolution of the phase transformation is described by the solution of a coupled differential equation system for (i) the compositional deviation X from the stoichiometric composition and for (ii) the degree of order S. The variables $X(\mathbf{r})$ and $S(\mathbf{r})$ are locally dependent on the position $\mathbf{r}$. Under irradiation the change rate of both variables follows [4,5]:

Composition:

$$\frac{\partial X}{\partial t} = D_0^{\mathrm{bal}}\phi\nabla^2 X + L(T,\phi)\nabla^2\left(\frac{\delta F(\{X,S,T\})}{\delta X} - \mu\right). \quad (1)$$

Degree of order:

$$\frac{\partial S}{\partial t} = -\varepsilon\phi S - M(T,\phi)\frac{\delta F(\{X,S,T\})}{\delta S}, \quad (2)$$

where ϕ is the atomic displacement rate due to the irradiation, $F(\{X,S,T\})$ is the thermodynamic potential, μ the chemical potential, $D_0^{\mathrm{bal}}, \varepsilon, L$ and M are positive constants related to the kinetics of the phase change, which depend on temperature T and ϕ. The first terms on the right-hand side of Eqs. (1) and (2) represent atomic diffusion and disordering due to ballistic jumps induced by irradiation. The second terms describe the thermodynamical forces which drive the system to the equilibrium state through the thermally activated jump processes. The thermodynamic potential $F(\{X,S,T\})$ is expressed in a Ginzburg–Landau form which contains the mean-field free energy density. It describes the phase separation by ordering and disordering processes coupled with spatial modulation of compositions. Details can be found in Refs. [4,5,10] where several examples of the stability of a tri-critical system with and without irradiation are treated. The steady-state solution defines the dynamical phase diagram which is shown in Fig. 1. It is essentially the phase diagram discussed by Martin and co-workers [2,3,11–13] for an ordered alloy under external forcing i.e. irradiation. An important example is the dissolution of an ordered precipitate in a disordered matrix at elevated temperatures. Eqs. (1) and (2) were solved one-dimensionally assuming an initial box-like profile of the composition and of the degree of order [4]. An example is shown in Fig. 2.

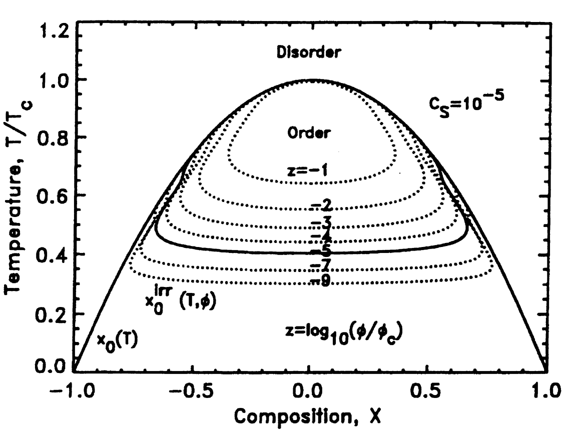

Fig. 1. The normalized dynamical phase diagram under irradiation calculated by the TDGL equation according to Ref. [4]. An ordered state exists below a critical temperature T$_c$ and for displacement rates smaller than ϕ_c.

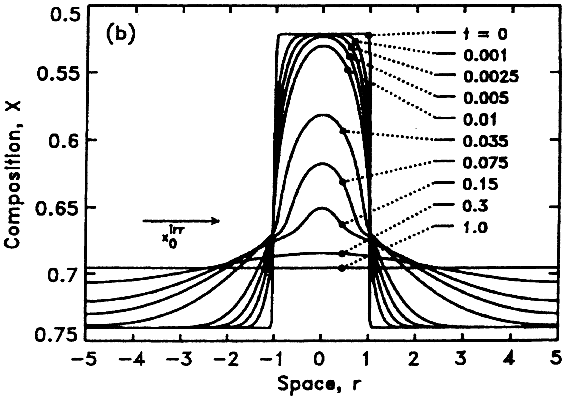

Fig. 2. Linear composition profile during the dissolution of an ordered precipitate calculated by solving the complete TDGL equation set (1) and (2) [4] (Various time steps in arbitrary units are indicated.)

For the purpose of this paper, only the final form of the TDGL equations may be given. If the higher order term $\nabla^4 X$ is neglected, the time evolution of the composition can be approximately written by

$$\frac{\partial}{\partial t} X = -\nabla \cdot \mathbf{J}_X(\mathbf{r}) \tag{3}$$

with an atomic flux

$$\mathbf{J}_X(\mathbf{r}) = -\left[D^{\mathrm{bal}} + D^{\mathrm{th}}(T,\phi) + bD^{\mathrm{th}} S^2(X)\right]\nabla X - bD^{\mathrm{th}} X \nabla S^2(X), \tag{4}$$

where the parameter b is a positive constant, and $D^{\mathrm{bal}} = D_0^{\mathrm{bal}}\phi$ and $D^{\mathrm{th}}(T,\phi)$ are the ballistic and the irradiation-enhanced diffusion coefficients, respectively. They generally depend on the atomic displacement rate ϕ and on temperature T.

From Eq. (4) it is seen that the ordering reaction influences the composition evolution in two ways: (i) it enhances the diffusion in the ordered state (first term) and (ii) it drives the concentration into the stoichiometric composition (second term). The second term is important at the phase boundary where ∇S^2 is large.

The degree of order follows a complex relation [4] $\partial S/\partial t = f(X^2, S, S^3, \nabla^2 S)$ which includes several parameters, e.g. the distance to the phase boundaries. The change rates of S and X are controlled by the atomic jumps. It is obvious that the state of order is much more sensitive to such jumps than the local composition, i.e. the equation for S can be eliminated by an adiabatic approximation. It is assumed that locally the state of order establishes a steady-state value $S_{\mathrm{st}}(X(\mathbf{r}))$ which depends on the slowly changing local composition $X(r)$. By setting $\partial S/\partial t = 0$, the homogeneous steady state of order inside the ordering phase field is [4]

$$S_{\mathrm{st}}^2(X) = \left\{ \begin{array}{ll} S_{\mathrm{st}}^2(0) * \left[1 - \left(\frac{X}{X_0^{\mathrm{irr}}}\right)^2\right] & \text{for} \quad X^2 \leqslant X_0^{\mathrm{irr}^2} \\ 0 & \quad\quad X^2 > X_0^{\mathrm{irr}^2} \end{array} \right\}, \tag{5}$$

where $S_{\mathrm{st}}(0)$ is the degree of order at the stoichiometric composition and X_0^{irr} the order–disorder line under irradiation (see Fig. 1). By irradiation the compositional interval of the ordered state is reduced as compared to the non-irradiated case ($S_{\mathrm{st}}^2 < S_{\mathrm{eq}}^2$ and $X_0^{\mathrm{irr}^2} < X_0^2$).

With Eqs. (4) and (5), the atom flux in adiabatic approximation has the form

$$\mathbf{J}_X(\mathbf{r}) = -D_{\mathrm{eff}}(X)\nabla X \tag{6}$$

with an effective, composition dependent diffusion coefficient

$$D_{\mathrm{eff}}(X) = D^{\mathrm{bal}} + D^{\mathrm{th}}\left[1 + bS_{\mathrm{st}}^2(X)\right]. \tag{7}$$

It will be shown below that these approximations result in similar composition profiles compared with profiles calculated by the application of the full set of TDGL equations.

3. Numerical solutions of the concentration equation in adiabatic approximation

Eqs. (6) and (7) were numerically integrated. The discontinuity at $X = X_0^{\mathrm{irr}}$ is erased by assuming a smooth transition of $S_{\mathrm{st}}^2(X)$ at $X = X_0^{\mathrm{irr}}$. The time evolution of 1-d (linear) and 3-d (radial-symmetric) problem was solved. The shape of the concentration profiles depends on the ratio of the diffusion coefficient inside and outside of the ordered precipitate $r = D_{\mathrm{eff}}(0)/D_{\mathrm{eff}}(X_0^{\mathrm{irr}})$. For $r = 1$, the effective diffusion coefficient is $D_{\mathrm{eff}} = D^{\mathrm{bal}} + D^{\mathrm{th}}$ and does not depend on the degree of order. The solution is a Gaussian diffusion profile. For $r > 1$, non-Gaussian profiles are obtained. Examples for $r = 10$ are shown in Figs. 3 and 4.

When Fig. 3 is compared with the exact solution of the TDGL system for the 1-d case according to Ref. [4] (see Fig. 2) it is obvious that the same behavior is observed as found in the exact calculations. There is a high solute concentration inside the ordered volume, a sudden decrease at the critical composition for the order–disorder transition and a smooth decrease outside the precipitate. This similarity allows us to apply the adiabatic approximation to the calculation of the composition profiles in 3-d case.

The 3-d solutions shown in Fig. 4 were calculated with the same parameters and time steps as in the linear case (Fig. 3). Two effects appear: (i) the composition gradients inside the ordered precipitate are larger than in the 1-d case and (ii) the time scale is changed. The radial symmetric solution evolves much faster than the linear solution as it is known for Gaussian profiles also. The effective diffusion coefficient must be corrected accordingly.

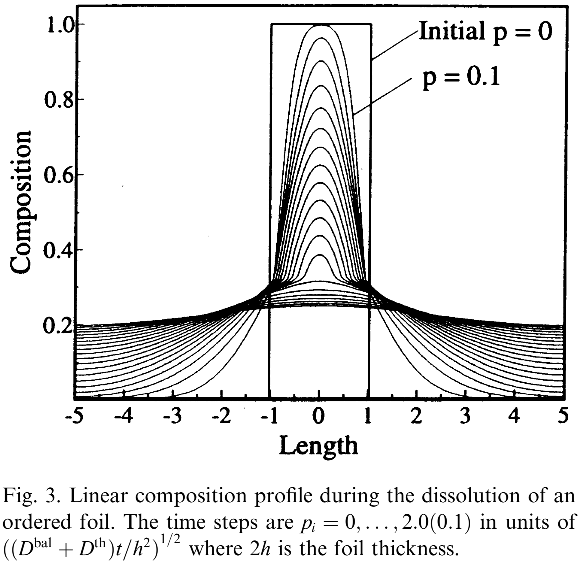

Fig. 3. Linear composition profile during the dissolution of an ordered foil. The time steps are $p_i = 0, \ldots, 2.0(0.1)$ in units of $((D^{\mathrm{bal}} + D^{\mathrm{th}})t/h^2)^{1/2}$ where $2h$ is the foil thickness.

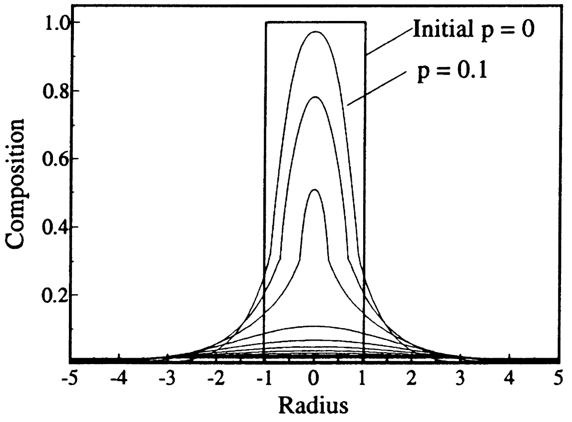

Fig. 4. Composition profile of a spherical, ordered precipitate during the dissolution under irradiation. The time steps are $p_i = 0,\ldots,1.0(0.1)$ in units of $((D^{\mathrm{bal}}+D^{\mathrm{th}})t/R^2)^{1/2}$, where R is the precipitate radius.

Generally, the results on the 3-d profiles confirm the general statements of Martin et al. [2] and Matsumura et al. [4,5] about the dissolution and disordering of ordered precipitates in disordered matrix. They will be used for the calculation of theoretical correlation coefficients for FIM-AP experiments.

4. Theoretical correlation coefficients from FIM-AP concentration profiles

We apply a statistical analysis of depth profiles obtained by FIM-AP developed for the investigation of multiphase materials [8,9]. It allows the calculation of the theoretical correlation coefficient $\rho_{\mathrm{AB}}^{\mathrm{th}}$ of the concentration profiles of two elements A and B for a presumed microstructure. These theoretical coefficients are then compared with experimentally observed correlation coefficients $\rho_{\mathrm{AB}}^{\mathrm{ex}}$. The method had been successfully applied to Gaussian-shaped composition profiles which are expected at lower irradiation temperatures when the precipitates dissolve in a disordered state [7]. For elevated temperatures, however, the calculation of theoretical correlation coefficients $\rho_{\mathrm{AB}}^{\mathrm{th}}$ has to take into account non-Gaussian-shaped composition profiles according to Fig. 4. The corresponding $\rho_{\mathrm{AB}}^{\mathrm{th}}$ are shown in Fig. 5 together with correlation coefficients $\rho_{\mathrm{AB}}^{\mathrm{th}}$(Gaussian) which are based on a Gaussian-shaped composition profile. The dissolution is scaled according to the dissolution parameter $\tau = 0.5(1+r)(D^{\mathrm{bal}}+D^{\mathrm{th}})t/R^2$, which becomes for $r = 1$ the standard scaling parameter for the dissolution of spherical precipitates $D_{\mathrm{Gauss}}t/R^2$ as it is used in the theory of diffusion [14]. From the figure it is seen that the correlation coefficients for the dissolution by a Gaussian profile or by a non-Gaussian profile differ especially at the early state of the disolution, when the participate is partially ordered. The curvature of $\rho_{\mathrm{AB}}^{\mathrm{th}}(\tau)$ changes for larger dissolution parameters τ where the precipitates is completely disordered $(X^2(r) < X_0^{\mathrm{irr}^2})$.

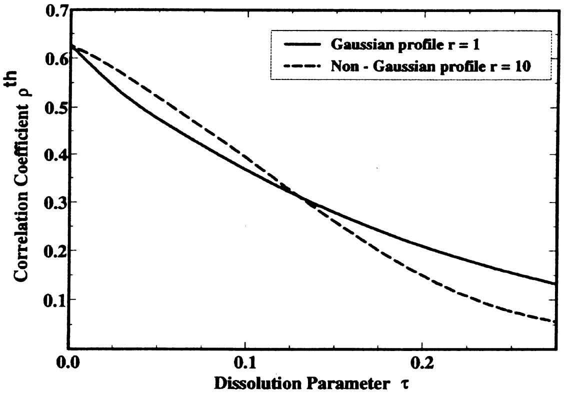

Fig. 5. Theoretical correlation coefficients $\rho_{\mathrm{AB}}^{\mathrm{th}}$(Non-Gaussian) for composition profiles ($r = 10$) according to Fig. 3(b) (see broken line) and $\rho_{\mathrm{AB}}^{\mathrm{th}}$(Gaussian) for a Gaussian profile ($r = 1$) (see solid line), respectively. The scale of the dissolution time is $\tau = 0.5(1+r)(D^{\mathrm{bal}}+D^{\mathrm{th}})t/R^2$.

Very different composition profiles can lead to equal correlation coefficients. Fig. 6 shows two examples of composition profiles of a spherical, ordered precipitate during the dissolution which have equal theoretical correlation coefficients $\rho_{\mathrm{AB}}^{\mathrm{th}} = \rho_{\mathrm{AB}}^{\mathrm{th}}(\mathrm{Gaussian}) = 0.3$ at $\tau = 0.1375$.

The deviations of $\rho_{\mathrm{AB}}^{\mathrm{th}}$ for different dissolution kinetics are only seen for short dissolution times. With the applied experimental techniques of FIM-AP [7], they could not be resolved directly. For the determination of actual depth profiles, the total volume fraction of the ordered material as measured by TEM was taken into account. An example is given in the next section.

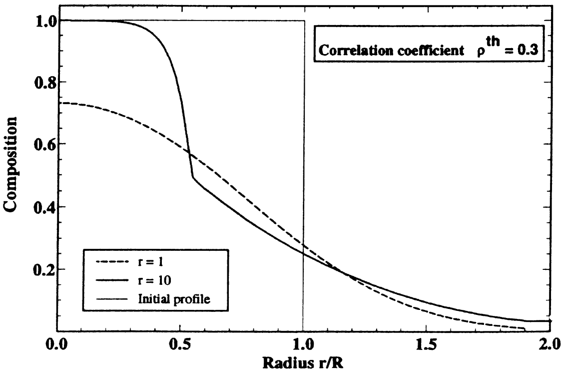

Fig. 6. Composition profiles of a spherical, ordered precipitate during the dissolution which have equal theoretical correlation coefficients $\rho_{\mathrm{AB}}^{\mathrm{th}} = \rho_{\mathrm{AB}}^{\mathrm{th}}(\mathrm{Gaussian}) = 0.3$ at $\tau = 0.1375$.

5. Discussion

We discuss the experimental correlation coefficients in the high temperature regime of the dissolution of ordered, spherical γ' precipitates measured in Nimonic PE16 under 300 keV Ni^+ ion irradiation. The initial size of the precipitates was $\overline{R} = 3.5$ nm. The experimental details are given in Ref. [7]. The analysis of the FIM-AP depth profiles after an irradiation fluence $\phi t = 10$ dpa at $T = 573$ K gave an experimental correlation coefficient $\rho^{\mathrm{ex}}_{\mathrm{AlTi}} = 0.17 \pm 0.07$. If we assume a Gaussian composition profile, a correlation coefficient $\rho^{\mathrm{th}}_{\mathrm{AB}}(\mathrm{Gaussian}) = \rho^{\mathrm{ex}}_{\mathrm{AB}} = 0.17$ corresponds to composition profile at $\tau = 0.235$ (see Fig. 5), i.e. the composition in the center at $R = 0$ reduced to about 50%.

Under the same irradiation conditions, TEM measurements were performed on similar material with the same precipitated volume fraction, but with larger precipitates ($\overline{R} = 10$ nm) [6]. Very strong intensities of the superlattice reflections were observed at 573 K and 10 dpa indicating that a large volume fraction of ordered material must be present. For a Gaussian profile, the scaled dissolution parameter for the larger precipitates is $\tau_{\mathrm{TEM}} = 0.235 * (3.5/10\ \mathrm{nm})^2 = 0.029$. The composition of the precipitate after an irradiation fluence 10 dpa is significantly reduced. A lower degree of order is expected which is at variance with the TEM results.

The discrepancy is resolved when a non-Gaussian composition profile such as that shown in Fig. 4 or Fig. 6 is assumed. With $\rho^{\mathrm{th}}_{\mathrm{AB}} = \rho^{\mathrm{ex}}_{\mathrm{AB}} = 0.17$, the profiles at scaled dissolution parameter $\tau = 0.19$ for the 3.5 nm precipitates and $\tau = 0.023$ for the 10 nm precipitates are obtained. After such short times, a larger volume fraction of ordered material is found in agreement with the strong intensities measured by TEM.

Interesting is the comparison of the diffusion coefficients obtained by the two composition profiles. Assuming a Gaussian composition profile at 10 dpa, the fit to the experimental data would give a diffusion coefficient $D_{\mathrm{Gauss}} = \tau R^2/\varphi t = 0.235 * 3.5^2/10\ \mathrm{dpa} = 0.29\ \mathrm{nm}^2/\mathrm{dpa}$. This value cannot be understood as it is much smaller than the ballistic diffusion coefficient $D^{\mathrm{bal}} \approx 1\ \mathrm{nm}^2/\mathrm{dpa}$ for such type of irradiation. As at such temperatures no spinodal type of decomposition with $D^{\mathrm{th}} < 0$ is expected in this system, an interpretation of the FIM-AP data by a Gaussian profile can be ruled out. However, the experiments do not allow the determination of the irradiation-enhanced diffusion coefficient D^{th} by assuming a non-Gaussian profile because the details of the composition profile at the phase boundary have to be taken into account. Further experimental work e.g. by means of the 3-d atom probe is needed.

6. Summary

The paper is summarized in the following statements:

- An adiabatic approximation is applied which allows the comparison of 1-d and 3-d composition profiles.
- Theoretical correlation coefficients are calculated for both 3-d Gaussian and non-Gaussian composition profiles.
- Comparison of the FIM-AP results with TEM data shows that under irradiation at low temperatures, ordered precipitates first disorder and then dissolve, but at elevated temperatures, the precipitates dissolve in an ordered state. The results confirm the calculations and predictions of the theories of Martin et al. [2,3] and Matsumura et al. [4,5].

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