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Journal of Nuclear Materials 251 (1997) 145–149

journal of nuclear materials

Instability of ordered precipitates due to local disordering and atomic mixing under irradiation

S. Matsumura *, M. Okudaira, C. Kinoshita

Department of Nuclear Engineering, Kyushu University 36, Fukuoka 812-81, Japan

Abstract

A time-dependent Ginzburg–Landau (TDGL) model for time-evolution of local degree of order S and local concentration X was employed in studying dissolution dynamics of ordered precipitates under irradiation with energetic particles. In the simulation, the irradiation effect was taken into account as random formation of small zones, in which disordering and atom mixing occur momentarily. The process depends sensitively on dose rate of irradiation. In the case of a high dose rate, the precipitates disappear in two separate steps. The ordered structure is quickly destroyed and then the precipitates dissolve into the matrix of a disordered phase. In comparison, the disordering and the dissolution proceed at the same time when the dose rate is significantly low. The precipitates with locally disordered regions shrink with time. Fine ordered precipitates are newly formed in the matrix in the latter case. It is suggested that the moderate irradiation with a low dose rate is available for refinement of ordered precipitates. © 1997 Elsevier Science B.V.

1. Introduction

The stability of ordered precipitates under particle irradiation is recognized as a relevant subject in the application of intermetallic alloys to nuclear technology [1]. When an alloy is exposed to irradiation with energetic particles, the external forces due to these particles act directly on the constituent atoms. The external forces often induce disordering and dissolution of initially ordered precipitates. Several theoretical attempts have been conducted to predict the stability of second-phase particles under irradiation up to now. Martin and his co-workers [2–4] have derived a kinetic master equation for phase transformation involved with the ballistic jumps of atoms due to irradiation and the thermally-activated motions. In their microscopic model, the free energy is formulated on the basis of the Bragg–Williams approximation in a discrete lattice system. On the other hand, the present authors [5,6] have proposed a more simplified mesoscopic description on the phase change concerned with ordering and phase separation induced by the external forces and/or the thermally activated atomic motions. A time-dependent Ginzburg–Landau (TDGL) model for ordering and phase separation [7] was extended to cover the radiation-induced phase change and coupled differential equations were derived for a spatially variable degree of order $S(r, t)$ and compositional modulation $X(r, t)$ in a continuous medium of an alloy. The theoretical argument mentioned above has been mainly based on a mean-field approximation to date. The kinetic behavior predicted by the mean-field models would be realized in the case of electron irradiation, where point defects are produced randomly over an irradiated area. In contrast, ion- or neutron irradiation often results in cascade formation where the lattice defects are produced collectively and locally. The mean field approximation should fail in some cases, such as on the discussion of microstructural change in two-phase alloys under ion or neutron irradiation.

The present paper treats our recent modification of the TDGL-model to include a stochastic process of local disordering and atomic mixing and reports preliminary results on the dissolution of ordered precipitates under irradiation.

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* Corresponding author. Tel.: +81-92 642 3772; fax: +81-92 642 3771/3800; e-mail: syo.tne@mbox.nc.kyushu-u.ac.jp.

PII S0022-3115(97)00266-3

2. Kinetic model for time-evolution of local composition and degree of order

The internal state of an alloy with an order–disorder transition is described by two continuous variables of composition X and degree of order S, which are dependent on position $\boldsymbol{r}$ and time t. If particle irradiation produces local damaged areas, the time evolution of phase transformation can be described as follows:

$$\frac{\partial X}{\partial t} = L(T, \phi)\nabla^2\left(\frac{\delta F(\{X, S, T\})}{\delta X} - \mu\right) + \theta(\boldsymbol{r}, \phi, t)D^{\mathrm{mix}}\nabla^2 X, \qquad (1)$$

and

$$\frac{\partial S}{\partial t} = -M(T, \phi)\frac{\delta F(\{X, S, T\})}{\delta S} - \theta(\boldsymbol{r}, \phi, t)M^{\mathrm{bal}}S, \qquad (2)$$

where ϕ is the atomic displacement rate due to the irradiation, $F(\{X, S, T\})$ is the thermodynamical potential, μ is the chemical potential, and L, M, D^{mix} and M^{bal} are positive constants related to the kinetics of the phase change: the thermal mobility of atoms, the ordering rate, the ballistic mixing coefficient and the ballistic disordering rate, respectively. The first terms in the right hand side of Eqs. (1) and (2) represent thermal processes of atomic motion approaching the equilibrium state. Following our previous treatment [5–7], the thermodynamical potential is expressed by a Ginzburg–Landau form,

$$F[\{X(\boldsymbol{r}), S(\boldsymbol{r}), T\}] = \int\left\{f(X, S, T) + \frac{H(T)}{2}(\nabla X)^2 + \frac{K(T)}{2}(\nabla S)^2\right\}\mathrm{d}\boldsymbol{r}, \qquad (3)$$

and the bulk free energy density $f(X, S, T)$ is given by

$$f(X, S, T) = f_0 + \frac{a(T)}{2}\left\{(X - x_{\mathrm{m}})^2 - b(T)\left\{x_0(T)^2 - X^2\right\}S^2 + b(T)^2 x_1(T)^2 S^4\right\}. \qquad (4)$$

Here, H and K are the interfacial energy coefficients for local fluctuation in X and S, f_0 is the mean-field free energy of the disordered phase with composition x_{m} and a, b and x_1^2 are positive constants depending on temperature T. $X = 0$ corresponds to the stoichiometric composition for the ordered structure. The thermal part of the kinetic equations has been described in detail in our previous papers [6,7].

On the other hand, the second terms in the right hand side of Eqs. (1) and (2) express ballistic mixing and disordering of atoms as local events within cascade damaged regions under irradiation. The shape function θ defines the damaged regions formed at time t, taking unity within these areas but otherwise zero. If $\theta = 1$ over the whole system, Eqs. (1) and (2) become identical to those derived in our previous study using the mean-field approximation [5,6].

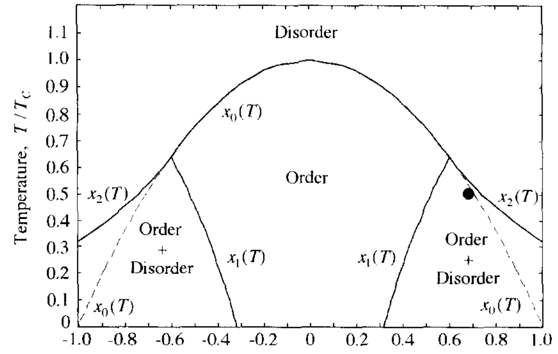

Fig. 1. Equilibrium phase diagram of the model system. The closed circle indicates the alloy simulated in the present work.

Fig. 1 shows an example of the equilibrium phase diagram derived from the bulk free energy given in Eq. (4). The parameter x_0 defined in Eq. (4) determines the order–disorder transition line. An ordered phase is formed around the stoichiometric composition $X = 0$ at temperatures below the critical point T_{c}. The order–disorder transition line ends in a tricritical point, below which the miscibility gap extends between ordered and disordered phases. The parameter x_1 presents the miscible limit of the ordered phase, when $x_1^2 < x_0^2$. The other side of the miscibility gap is given by x_2, where $x_2^2 = (x_0^2 + x_1^2)^2/4x_1^2$.

3. Simulation procedure

The closed circle plotted in Fig. 1 indicates the system concerned with the present simulation, where a one-dimensional array of 1000 cells was assumed with a periodic boundary condition. The initial state was considered to contain an ordered precipitate embedded in the disordered matrix in thermal equilibrium at $T = 0.5T_{\mathrm{c}}$. The simulation of dissolution behavior of the precipitate under irradiation was carried out on the basis of the kinetic equations, Eqs. (1) and (2), with a finite-difference approximation for both the spatial and temporal derivatives. For simplicity, the thermal and the ballistic parts of atomic motion were handled separately. In a unit time interval Δt, the irradiation at first produces damaged regions with a given probability W. Each cell was allotted a random number R between 0 and 1 generated in a computer. The positions of the regions were determined where $R < W$. The value W also defines the probable number $\langle N \rangle$ of damaged regions formed per one step of time interval Δt, as $\langle N \rangle = 1000W$. The parameter $\langle N \rangle$ is regarded as being proportional to ϕ. The size of the regions was set to be 3 cells in the present calculation. We assumed that the complete disordering

($S_i \to 0$) and the homogenization in concentration ($X_i \to \Sigma_{i=1}^{3} X_i/3$) occur within the damaged regions at the same time as their formation. Following the production of damaged regions, the thermal relaxation proceeds for the finite time interval Δt, according to

$$\frac{\partial X}{\partial t} = La\nabla^2 X - LH\,\nabla^4 X + Lab\nabla^2(XS^2), \tag{5}$$

and

$$\frac{\partial S}{\partial t} = Mab\left(x_0^2 - X^2\right)S - 2Mab^2 x_1^2 S^3 + MK\,\nabla^2 S, \tag{6}$$

which are obtained by inserting Eqs. (3) and (4) into the first terms in the right hand side of Eqs. (1) and (2). The parameters L and M used were the same as those in previous studies [5]. The above procedure of simulation was repeated given times I. The unit time interval Δt was set so as to avoid spurious solutions.

4. Results and discussion

Fig. 2 shows the time evolution of the dissolution of an ordered precipitate when $\langle N \rangle = 10$. The upper and lower rows give temporal changes in X and S, respectively. In the initial state, an ordered precipitate with $X = 0.52$ and $S = 0.51$ is located in the center and the rest part is the disordered phase with $X = 0.74$. The disordering in the precipitate proceeds rapidly with particle irradiation. One can see local fluctuation of concentration within the precipitate at $I = 100$ in Fig. 2(b). This fluctuation of X is coupled with local change in degree of order. At $I = 1 \times 10^3$ in Fig. 2(c), the precipitate has been fully disordered. The local fluctuation in X within the precipitate has disappeared because there is no longer local change in S. The profile of X at this time is almost identical to that in the initial stage. The precipitate and the matrix still keep their initial concentrations until this stage and they are well distinguished from each other with sharp interfaces. The precipitate dissolves into the matrix in the following late stage, as shown in Fig. 2(d) for $I = 1 \times 10^6$. Thus, one can recognize two separate stages of disordering and dissolution in the process demonstrated in Fig. 2.

Fig. 3 illustrates the process when the dose rate is reduced to $\langle N \rangle = 1$ at the same temperature. The precipitate finally dissolves into the matrix under this condition also, as shown in Fig. 3(d). However, the disordering and the dissolution proceed simultaneously in the intermediate stage. The interfaces between the precipitate and the matrix have become broad considerably when the disordering in the precipitate has been almost completed, as can be seen in Fig. 3(c).

If the dose rate is further reduced to $\langle N \rangle = 0.1$, the precipitate dissolves only partly, as shown in Fig. 4, since the thermal relaxation in the damaged areas may play a considerable role. Small disordered zones have been formed in the precipitate at $I = 10^5$, accompanied with local fluctuations in X, as shown in Fig. 4(b). The concentration gradient beside the precipitate suggests that the precipitate is slightly dissolving into the matrix. However, the interfaces between the precipitate and the matrix are still well-defined. A fine precipitate has been newly formed in the matrix in Fig. 4(c) at $I = 10^6$. Prolonged irradiation leads to the shrinkage of the pre-existing precipitate, but also to the nucleation of finer ordered zones, as shown in Fig. 4(d). One can consider that the final stationary state will involve fine ordered precipitates uniformly dispersed in the disordered matrix.

Here, the process of dissolution of an ordered precipitate under irradiation has been investigated in Figs. 2–4 as

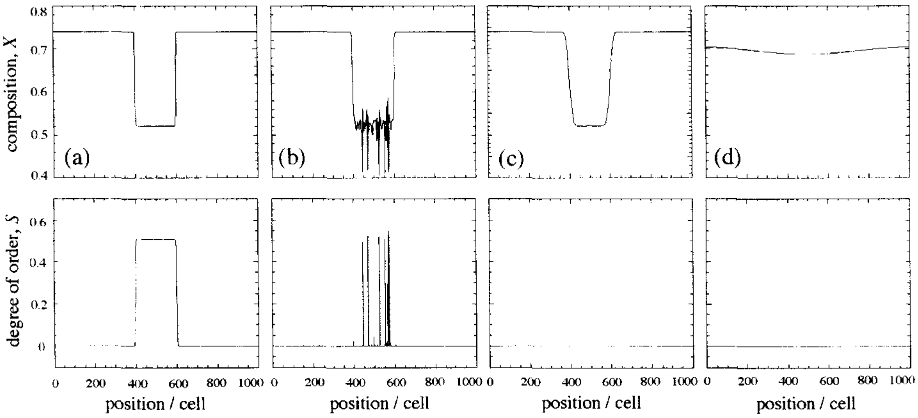

Fig. 2. Temporal evolution of dissolution of an ordered precipitate when $\langle N \rangle = 10$. The initial state (a), $I = 100$ (b), $I = 10^3$ (c) and $I = 10^6$ (d). The upper and bottom rows illustrate spatial variations of X and S, respectively.

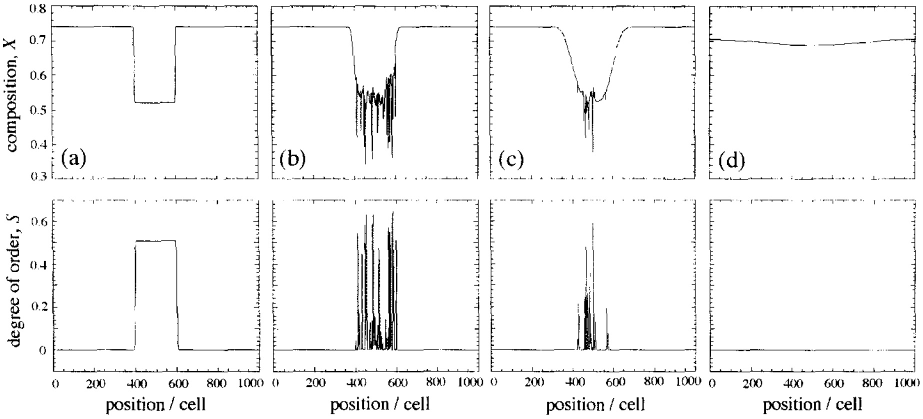

Fig. 3. Temporal evolution of dissolution of an ordered precipitate when $\langle N \rangle = 1$. The initial state (a), $I = 10^3$ (b), $I = 10^4$ (c) and $I = 10^6$ (d). Note that the amounts of fluence for (b) and (c) are same as those for (b) and (c) in Fig. 2.

a function of $\langle N \rangle$ or dose rate. These results however may also show qualitatively temperature dependence of the process at a given dose rate, since the relative magnitude of ballistic transport of atoms to the thermally-activated motion is a dominant factor controlling the kinetic behavior in the present simple model [5,6]. At a significantly high dose rate or a low temperature, ordered precipitates disappear in two separate steps, as shown in Fig. 2. The ordered structure is quickly destroyed and then the precipitates dissolve into the matrix of a disordered phase. The two-stage process has been experimentally recognized in Nimonic PE16 irradiated with 300 keV Ni^+ ions at room temperature [8,9] and has been also predicted by previous theoretical studies based on the mean-field approximation [2–7]. In contrast, the disordering and the dissolution proceed at the same time when the dose rate is significantly low, or at a high temperature. The precipitates with locally disordered regions shrink with time, and fine ordered precipitates are newly formed in the matrix, as shown in Fig. 4. The previous mean-field treatments [2–7] have revealed the shrinkage of ordered precipitates with sharp interfaces with increase of fluence, but not the formation of fine precipitates. The refinement of ordered precipitates under particle irradiation has been experimentally observed in various systems such as Ni–Al [10,11], Ni–Al–Ti [12] Nimonic PE-16 alloys [11,13]. The result given in Fig. 4 suggests that the moderate irradiation with a low dose rate would be available for refinement of ordered precipitates or controlling the size and dispersion of them. The localized disordering and atomic mixing induced by irradiation should be taken into account in detailed discussion on microstructural change in two-phase alloys. We are now carrying out more systematically extended study of the processes in the higher dimensional space. The results will be reported elsewhere in the near future.

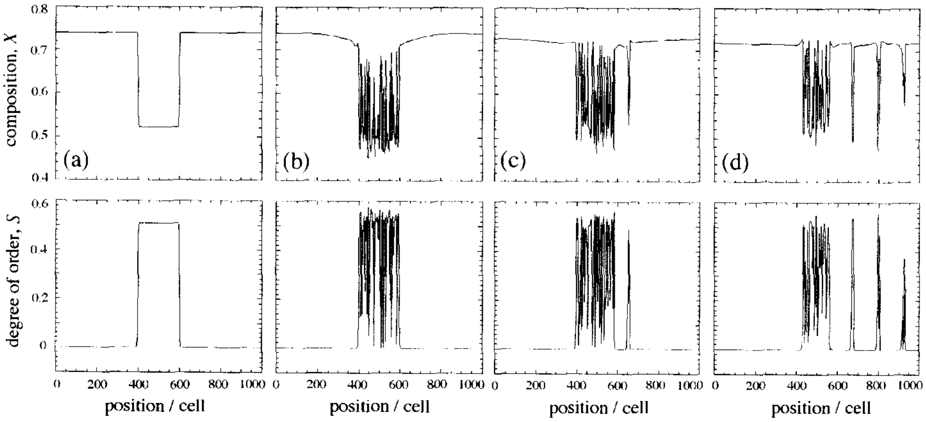

Fig. 4. Structural change when $\langle N \rangle = 0.1$ is assumed. The initial state (a), $I = 10^5$ (b), $I = 10^6$ (c) and $I = 6 \times 10^6$ (d). The pre-existing precipitate is being redivided into finer ones.

5. Summary

The present paper has illustrated our recent trial of the phenomenological time-dependent Ginzburg–Landau (TDGL) formulation on the kinetics of disordering and dissolution of ordered precipitates under irradiation. Here, the irradiation effect has been treated as a stochastic process of random formation of small zones, in which disordering and atom mixing occur momentarily. The preliminary results of these simulations have demonstrated that in the case of a high dose rate, the ordered structure is quickly destroyed and then the precipitates dissolve into the disordered matrix. In contrast, the disordering and the dissolution proceed at the same time when the dose rate is significantly low. Fine ordered precipitates are newly formed in the matrix in the latter case.

Acknowledgements

This study was partly supported by the Grants-in-Aid for Scientific Research B (#07455260) and for Scientific Research on the Priority Area 'Mechanisms of Phase Transformations for the Structure Control of Materials' (#09242234) from the Ministry of Education, Science, Sports and Culture (Monbusho) of Japan.

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