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Analytical model of radiation-induced precipitation at the surface of dilute binary alloy

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Abstract

Growth of precipitate layer at the foil surface of an undersaturated binary alloy under uniform irradiation is treated analytically. Analytical expressions for the layer growth rate, layer thickness limit and final component concentrations in the matrix are derived for coherent and incoherent precipitate–matrix interfaces. It is shown that the high temperature limit of radiation-induced precipitation is the same for both types of interfaces, whereas layer thickness limits are different. A parabolic law of the layer growth predicted for both types of interfaces is in agreement with experimental data on γ'-phase precipitation at the surface of Ni–Si dilute alloys under ion irradiation. Effect of sputtering on the precipitation rate and on the low temperature limit of precipitation under ion irradiation is discussed.

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1. Introduction

One of the consequences of radiation-induced segregation (RIS) in alloys is the formation and growth of a radiation-induced phase layer near point defect (PD) sinks in undersaturated solid solutions [1]. This phenomenon has been studied both experimentally [2–10] and theoretically [11–15] with a major emphasis on Ni–Si alloys under electron or ion irradiation. In analytical treatments of precipitation under irradiation [13–15] only a supersaturated solid solution (Ni–12.7at.%Si), where the precipitation is a radiation-enhanced process, has been considered using a number of simplifications: precipitation on the surface of a semi-infinite sample, transport of solute atoms to the phase layer only by mobile and tightly bound interstitial–solute complexes.

In the present paper an analytical model for phase layer growth kinetics at the surface of undersaturated binary alloy is developed taking into account RIS via interstitial and vacancy mechanisms. Precipitation at foil surfaces under uniform irradiation is considered for coherent and incoherent precipitate–matrix interfaces. Predicted for these interfaces layer growth rates, layer thickness limits and final solute concentrations in equilibrium with the phase layer are compared. Effect of sputtering on precipitation under ion irradiation is discussed.

2. Incoherent precipitate–matrix interface

Firstly let us consider the growth of an incoherent phase layer at the surface of a foil of 2 L in thickness in an undersaturated binary alloy with the solute content C_{A0}. In this case the interface is a perfect sink for PD. Under irradiation a region of the thickness R of the order of PD free path [16] forms near the interface, where PD concentration gradients are significant and RIS of components operates. The value of R is determined by the alloy microstructure and irradiation conditions as follows [16]:

$$R = \sqrt{\frac{2(\langle C_{v0}\rangle - C_{ve})D_{v0}}{K}},$$

$$\langle C_{v0}\rangle = 0.5\left(\sqrt{\frac{4K}{\mu_R D_{v0}} + \left(\frac{\rho_s}{\mu_R}\right)^2} - \frac{\rho_s}{\mu_R}\right) + C_{ve}, \tag{1}$$

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where $\langle C_{v0}\rangle$ and D_{v0} are the average concentration and diffusivity of vacances in the irradiated alloy, respectively, ρ_s is the total PD sink strength, C_{ve} is the vacancy thermal equilibrium concentration, μ_R is the vacancy–interstitial recombination coefficient, K is the generation rate of freely migrating PD.

Further we consider alloys, in which RIS leads to the enrichment of a solute near the specimen surface. When the solubility limit C_A^e is exceeded, a layer of radiation-induced phase begins to grow even in undersaturated solid solution. During this process the solubility limit C_A^e is maintained near the interface. Irradiation times are considered below, at which the equality is established between j_A, the diffusion flux of component A from the matrix into the region R and that J_A inside the region R towards the interface. It is supposed that the layer growth is limited by the flux j_A until the late stage, when the growth becomes limited by the flux J_A caused by RIS. At this late stage the flux J_A is assumed to be steady-state one J_A^s. It is taken into account that PD fluxes do not change significantly during the component redistribution due to RIS in the R-region [16]. In this case usual equations for steady-state concentrations of vacancies C_v, interstitials C_i and steady-state solute flux J_A^s can be used [1,16]:

$$-D_{\beta 0}\nabla C_{\beta 0} = -D_\beta \nabla C_\beta + (d_{A\beta} - d_{B\beta})C_\beta \alpha \nabla C_A, \tag{2}$$

$$J_A^s = -D_A \alpha \nabla C_A + C_A(d_{Av}\nabla C_v - d_{Ai}\nabla C_i), \tag{3}$$

where the diffusion coefficients of components D_k ($k = A, B$) and PDs D_β ($\beta = v, i$) are equal to $D_k = d_{ki}C_i + d_{kv}C_v$, $D_\beta = \sum_k d_{k\beta}C_k$, $d_{k\beta}$ are the component diffusivities via vacancy ($\beta = v$) and interstitial ($\beta = i$) mechanisms, α is the thermodynamic factor, the index '0' relates to an alloy without RIS.

From Eqs. (2) and (3) one can obtain the following equation for the solute concentration profile $C_A(r)$:

$$\begin{aligned} &J_A^s D_v D_i + \alpha \nabla C_A (d_{Av}d_{Ai}C_A D_A + d_{Bv}d_{Bi}C_B D_B) \\ &\quad = D_{v0}\nabla C_{v0} C_A C_B (d_{Av}d_{Bi} - d_{Bv}d_{Ai}). \end{aligned} \tag{4}$$

Using the notations $y = r/R$, $z(y) = C_A(y)/(1 - C_A(y))$ and omitting the details of derivation one can write the following approximate solution of Eq. (4):

$$\begin{aligned} z(y) = z_0(y)\Bigg\{1 + \left(\frac{z^e}{z_0(0)} - 1\right)\int_y^1 \frac{\mathrm{d}x}{C_{v0}(x)z_0(x)} \\ \Bigg/ \int_0^1 \frac{\mathrm{d}x}{C_{v0}(x)z_0(x)}\Bigg\}, \end{aligned} \tag{5}$$

where

$$z_0(y) = z_{01}(C_{v0}(y)/\langle C_{v0}\rangle)^{(b/\alpha a)};$$
$$z^e = C_A^e/(1 - C_A^e); \quad z_{01} = \lambda/(1 - \lambda),$$

$$a = \left(d_{Av}d_{Bv}D_{i0}^2 + d_{Ai}d_{Bi}D_{v0}^2\right)/D_{v0}D_{i0}, \quad b = d_{Av}d_{Bi} - d_{Bv}d_{Ai},$$

$$J_A^s = \frac{a\alpha}{D_{i0}R}\left(\frac{z^e}{z_0(0)} - 1\right)\Bigg/\int_0^1 \frac{\mathrm{d}x}{C_{v0}(x)z_0(x)}. \tag{6}$$

In Eq. (5) $\lambda = C_A(1)$ is the time dependent quasi steady-state solute concentration on the R-region boundary. Steady-state PD concentration profiles $C_{\alpha 0}(r)$ near various PD sinks including sample surfaces have been obtained in Ref. [16]. It follows from the Eq. (6), that the quasi-steady-state solute flux J_A^s depends on irradiation conditions, alloy microstructure, difference in component diffusivities via vacancy and interstitial mechanisms as well as on the solute concentration $\lambda(t)$ on the R-region boundary.

An analysis shows that after the onset of irradiation the value of $\lambda(t)$ begins to decrease from its initial value C_{A0}, the flux J_A decreases and J_A increases with time. After some transient period, t_0, these fluxes become equal. Then, the phase layer growth proceeds provided the equality $J_A = j_A$ is maintained, whereas $\lambda(t)$ changes slowly and reaches a limit $\lambda_m < C_{C0}$ at longer irradiation times. Then the layer thickness, $l(t)$, reaches the maximum value l_m and the solute concentration $C_A(r)$ in the matrix outside the R-region becomes uniform and equal to $\lambda_m = C_A^{ir}$. Since the R-region is shifted into the foil interior together with the precipitate–matrix interface during the layer growth, then for $t \geqslant t_0$

$$\left(C_A^P - \lambda(t)\right)\dot{l}(t) = J_A = j_A, \tag{7}$$

where C_A^P is the solute atom concentration in the phase layer.

Using an approximate solution of the diffusion equation for $C_A(r, t)$ in the matrix outside the R-region derived in Ref. [17], one can obtain the following:

$$\int_{t_0}^t j_A(\tau)\,\mathrm{d}\tau = (C_{A0} - \lambda(t))S(t) - (C_{A0} - \lambda(t_0))S(t_0)L, \tag{8}$$

$$S(t) = 1 - \exp\left(-2\sqrt{D_A t/\pi L^2}\right), \tag{9}$$

where D_A is the radiation-enhanced diffusion coefficient of solute atoms in the matrix interior, where PD concentration gradients are absent ($r > R$).

Usually inequalities $C_A^P \gg C_{A0} > \lambda_m$ are valid for undersaturated alloys. Therefore, one can approximately replace $C_A^P - \lambda(t)$ by $C_A^P - \lambda_m$ in Eq. (7). In this case

$$\begin{aligned} \left(C_A^P - \lambda_m\right)(l(t) - l_0) = ((C_{A0} - \lambda(t))S(t) \\ - (C_{A0} - \lambda(t_0))S(t_0))L, \end{aligned} \tag{10}$$

where l_0 is the thickness of the layer formed during transient period t_0.

An approximate solution of Eq. (10) at times $t \gg t_0$ can be obtained by replacing $\lambda(t)$ with $\lambda_{\mathrm{m}} = C_A^{ir}$:

$$l(t) \approx L\frac{\left(C_{A0} - C_A^{ir}\right)}{\left(C_A^{\mathrm{P}} - C_A^{ir}\right)}S(t). \tag{11}$$

Let us introduce a characteristic diffusion time $t_L = \pi L^2/4D_A$. Then for t in the interval $t_0 \ll t \ll t_L$, Eq. (11) is reduced to

$$l(t) \approx \frac{\left(C_{A0} - C_A^{ir}\right)}{\left(C_A^{\mathrm{P}} - C_A^{ir}\right)}\sqrt{D_A t}. \tag{12}$$

According to Eq. (12), the phase layer thickness depends parabolically on irradiation time. It should be noted that the same layer growth law can be derived with a more accurate approach by taking into account the time dependence of $\lambda(t)$ in Eq. (10). This approach consists in inserting Eq. (6) for J_A^{s} in Eq. (7) and deriving $\lambda(t)$ as a function of l. Then Eq. (10) is reduces to the differential equation of the first order for $l(t)$, which has the solution given by Eq. (12) in the range of $t_0 \ll t \ll t_L$. This work is now in progress.

The layer thickness increases until an equilibrium between the layer and the matrix interior is achieved. The equilibrium solute concentration C_A^{ir} can be obtained from the condition of vanishing the steady-state solute flux J_A^{s} (Eq. (6)) considering that $C_A^{ir} \ll 1$ in undersaturated alloys. The layer thickness limit l_{m} can be found from Eq. (11) at $t \to \infty$ or from the conservation law for component A:

$$l_{\mathrm{m}} = L\frac{\left(C_{A0} - C_A^{ir}\right)}{\left(C_A^{\mathrm{P}} - C_A^{ir}\right)}, \quad C_A^{ir} = \frac{z^{\mathrm{e}}}{\delta}, \quad \delta = \left(\frac{C_{v\mathrm{e}}}{\langle C_{v0}\rangle}\right)^{b/\alpha a}. \tag{13}$$

Actually, $C_A^{ir} = z^{\mathrm{e}}/\delta$ determines the radiation-modified phase diagram of a binary alloy with incoherent precipitate–matrix interface, i.e. the minimum solute concentration C_{A0}, above which the precipitation occurs at the specimen surface in undersaturated alloys under irradiation.

3. Coherent precipitate–matrix interface

This interface is assumed not to be a PD sink. Therefore, RIS of alloy components occurs near the specimen surface in the R-region in the initial period of irradiation and in the region $l(t) \leqslant r \leqslant R$ after the precipitate layer formation. Since RIS is the driving force for precipitation in undersuturated alloys, the precipitate layer thickness limit l_{m} can not exceed R.

As in the previous case, it will be assumed in the following that the solubility limit C_A^{e} is maintained on the interface. Then Eqs. (2)–(4) are valid in the range $l(t) \leqslant r \leqslant R$, and for $y_l \leqslant y \leqslant 1$, where $y_l = l/R$, the approximate solution of these equations can be written in the following form:

$$z(y) = z_0(y)\left\{1 + \left(\frac{z^{\mathrm{e}}}{z_0(y_l)} - 1\right)\int_y^1 \frac{\mathrm{d}x}{C_{v0}(x)z_0(x)} \Bigg/ \int_{y_l}^1 \frac{\mathrm{d}x}{C_{v0}(x)z_0(x)}\right\}, \tag{14}$$

$$J_A^{\mathrm{s}} = \frac{a\alpha}{D_{i0}R}\left(\frac{z(y)}{z_0(y)} - 1\right) \Bigg/ \int_{y_l}^1 \frac{\mathrm{d}x}{C_{v0}(x)z_0(x)}. \tag{15}$$

As in the Section 2, irradiation times $t > t_0$ are considered when a growth of the precipitate layer proceeds under the condition $J_A = j_A$. However, in contrast to the previous case, the R-region does not shift towards the matrix interior in distinction to the precipitate–matrix interface. Thus, only RIS in the region $y_l \leqslant y \leqslant 1$ is responsible for the precipitation and should be accounted for. The solute concentration $\lambda = C_A(1)$ on the R-region boundary is a function of time and layer thickness, $\lambda(t, l)$ along with its limit λ_{m} (l_{m}), which is equal to the equilibrium solute concentration C_A^{ir} (l_{m}). As before, the latter can be obtained from the condition of vanishing the steady-state solute flux J_A^{s} (Eq. (15)), and the layer thickness limit l_{m} can be obtained from the law of A-component conservation:

$$C_A^{ir} = \frac{z^{\mathrm{e}}}{\varepsilon(l_{\mathrm{m}})}, \quad l_{\mathrm{m}} \approx L\frac{\left(C_{A0} - C_A^{ir}\right)}{\left(C_A^{\mathrm{P}} - C_A^{ir}\right)}, \quad \varepsilon(l_{\mathrm{m}}) = \left(\frac{C_{v0}(l_{\mathrm{m}}/R)}{\langle C_{v0}\rangle}\right)^{b/\alpha a}. \tag{16}$$

The system of Eq. (16) for C_A^{ir} and l_{m} can be solved numerically. It should be noted that Eq. (16) for C_A^{ir} at $l_{\mathrm{m}} = 0$ reduces to Eq. (13) and determines the minimum solute content C_{A0}, above which the precipitation occurs. So, the high temperature limit of radiation-induced precipitation is given by Eq. (13) for both types of precipitate–matrix interfaces.

An analysis similar to the one made in Section 2 (Eqs. (8)–(10)) results in the following equation for $l(t)$:

$$\left(C_A^{\mathrm{P}} - \lambda_{\mathrm{m}}\right)(l(t) - l_0) = ((C_{A0} - \lambda(l,t))S(t) - (C_{A0} - \lambda(t_0))S(t_0))L. \tag{17}$$

Further, let us consider a thick foil ($C_{A0}L \gg C_A^{\mathrm{P}}R$) and longer times $t \gg t_0$. In this case $\lambda(l,t) \to z^{\mathrm{e}}/\varepsilon(l)$. Using an expression for $C_{v0}(y)$ from Ref. [16] and inserting it in $\varepsilon(l)$ one can reduce Eq. (17) to the following one:

$$y_l + \left(2y_l - y_l^2\right)^{|b/\alpha a|}S(t)/\beta = C_{A0}S(t)/z^{\mathrm{e}}\beta, \tag{18}$$

where $\beta = (C_A^{\mathrm{P}} - \lambda_{\mathrm{m}})R/z^{\mathrm{e}}L$.

A parabolic layer growth law follows from Eq. (18) at times $t < t_{\mathrm{p}}$, until the first term on the left hand side (lhs) of Eq. (18) is larger than the second term. One can estimate a characteristic time t_p by equating the first and the second terms in lhs of Eq. (18). If an alloy is relatively dilute and $l_m \ll R$, then

$$t_p \approx \frac{t_L}{4}\left(\frac{C_A^P R}{C_{A0} L}\right)^2 \left(\frac{C_{A0}}{z^e}\right)^{2|\alpha a/b|}. \tag{19}$$

So, at $t_p \ll t_L$ for a thick foil, t_p is not dependent on L. At $t = t_p$ the layer thickness reaches a value of the order of l_p:

$$l_p \approx (R/2)(C_{A0}/z^e)^{|\alpha a/b|}. \tag{20}$$

By determining l_m from $C_A^{ir} = z^e/\varepsilon(l_m)$ one obtains:

$$l_m/l_p = \left(C_A^{ir}/C_{A0}\right)^{|\alpha a/b|}/(1 - l_m/2R). \tag{21}$$

Since $C_A^{ir} \approx C_{A0}$ for a thick foil, the most part of l_m grows with a parabolic law during the time interval $t_p \ll t_L$, thereafter the layer thickness proceeds to increase slowly and the concentration of A-component in the matrix becomes uniform and equal to C_A^{ir}. A more detailed analysis for an application to dilute Ni–Si alloys is now in progress.

4. Discussion

From above treatment it follows that the kinetics of radiation-induced precipitation at the surfaces of undersaturated binary alloy foil reveals both common features as well as essential distinctions in the cases of coherent and incoherent precipitate–matrix interfaces.

One of the common features is the criterion of precipitation (Eqs. (13) and (16) for C_A^{ir} at $l_m = 0$). In fact, this criterion is the condition of vanishing the flux of solutes towards the specimen surface at the start of irradiation or the condition $C_A^s = C_A^e$, where C_A^s is the steady-state solute concentration setting up at the specimen surface due to RIS. A similar condition has been employed earlier in Refs. [18,19] in an analysis of temperature ranges of radiation-induced and radiation-retarded precipitate stability in austenitic steels. If the solute content C_{A0} exceeds C_A^{ir}, the equilibrium solute concentration under irradiation, then the precipitate layer forms after a time t_s, needed for the solute concentration near the specimen surface to reach the solubility limit C_A^e due to RIS. The time t_s can be estimated numerically [12,20].

The model developed above predicts a parabolic dependence of the layer thickness on irradiation time in the interval $t_0 \ll t \ll t_L$ for both types of precipitate–matrix interfaces followed by the growth saturation at $l = l_m$. However, for a thick foil the characteristic times-to-growth-saturation are different. For the incoherent interface this time is t_L and depends on L, whereas for the coherent interface it is equal to t_p and does not depend on L (the last estimate is applicable for a semi-infinite sample as well). For the growth of coherent γ'-phase (Ni_3Si) on the surface of ion irradiated Ni–6at.%Si and Ni–1at.%Si alloys such a parabolic law has been observed [9,13]. In addition, such a layer growth law was revealed in dilute Ni–Si alloys by numerical calculations [12].

The precipitate layer thickness limits l_m are different for the precipitate–matrix interfaces considered. For the coherent interface l_m does not exceed the R-region width. Such a conclusion is valid also for other PD sinks (grain boundaries, voids, dislocation loops).

It should be noted that sputtering of surface atoms under irradiation with low energy ions may influence seriously the layer growth rate. The effect of sputtering can be roughly estimated by differentiating Eq. (12) or (17) and by taking the sputtering rate to have the following simple form: $u_s = IS_p/N$, where I is the ion flux, N the atomic density of sputtered material, S_p the sputtering coefficient depending on the target material as well as on the type and energy of ions. Then for $t_0 < t \ll t_L$ one can write the following equation:

$$\dot{l}(t) \approx \frac{\left(C_{A0} - C_A^{ir}\right)}{2\left(C_A^P - C_A^{ir}\right)}\sqrt{\frac{D_A}{t}} - u_s. \tag{22}$$

Since u_s depends only weakly on temperature and D_A decreases rather sharply with decreasing the temperature, the effect of sputtering on the precipitation rate is more pronounced at low temperatures. Moreover, by putting $\dot{l}(t_0) = 0$ in Eq. (22) one can estimate the low temperature limit of radiation-induced precipitation (the high temperature limit is determined by Eq. (13)). The existence of both low and high temperature limits for radiation-induced γ'-phase precipitation at PD sinks (mainly dislocation loops) under electron and ion irradiation has been discussed earlier in Refs. [1,3].

5. Conclusions

An analytical model for the radiation-induced phase layer growth on foil surfaces of undersaturated binary alloys has been developed taking into account the RIS. In the cases of coherent and incoherent precipitate–matrix interfaces the layer thickness depends on irradiation time t as $\sim\sqrt{t}$ after an initial incubation period, in agreement with experimental data on γ'-phase growth on the surface of ion irradiated dilute Ni–Si alloys. At longer t the layer thickness tends to saturate on a level and in a characteristic time both depending on the type of precipitate–matrix interface, the layer thickness limit for the coherent interface does not exceed a value of the order of PD free path. The high temperature limit of radiation-induced precipitation is the same for both types of interfaces, whereas final component concentrations in equilibrium with the phase layer are different.

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