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Contribution of dissipative processes to radiation-induced solid-solution instability

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It is shown that a binary solid solution under irradiation may become unstable when vacancy-interstitial mutual recombination takes place, while it would be (linearly) stable in the absence of recombination, for the same average defect concentration. The general conditions for this to occur are elucidated and are not very restrictive. Available models for solid solutions under irradiation may exhibit the predicted loss of stability. This points to the possibility of radiation-*induced* precipitation being an example of the formation of dissipative structures in solids.

I. INTRODUCTION

There is growing evidence that irradiation by energetic particles may not only destroy preexisting second-phase precipitates, or accelerate second-phase precipitation in supersaturated alloys, but also *induce* second-phase precipitation in *undersaturated* solid solutions (for recent reviews and discussions see Refs. 1,2).

The clearest evidences for the latter process are listed in Table I. In the particular case of Ni-Si, Ni-Ge,[3] and[4] Al-Zn undersaturated solid solutions, it could be established that the solvus temperature is a function of the irradiation *flux*. The irradiation *flux* (and not the integrated dose) therefore appears as an extra control parameter of the state of a solid solution under irradiation, thus providing an example in favor of a more general statement by Adda, Beyeler, and Brebec.[5]

As shown by several authors[6-8] it is difficult to account for the formation of the observed second phases in undersaturated solid solutions by the alteration of the free energy of the system by irradiation-sustained point-defect supersaturation. On the other hand, several mechanisms for radiation-induced precipitation have been proposed, where the key role is played by the nonconservative nature of the point defects. Such is the case for the growth models of incoherent precipitates under irradiation[9,10]. Point-defect *elimination* (or creation) at the precipitate-matrix interface is a prerequisite for a shift of the solvus temperature under irradiation. Such is also the case for the models of radiation-induced precipitation at point-defect sinks, where the precipitation process is a consequence of the drag of the solute by the *point-defect fluxes* towards the sinks (for review and discussion, see Refs. 11,12). Similarly in the available model of radiation-induced formation of coherent precipitates,[4] vacancy-interstitial *mutual recombination* at the precipitate is a necessary condition for the proposed mechanism to operate.

In all the above models, the *dissipative processes* sustained by irradiation (point-defect fluxes, and recombination reactions) drive the precipitation process. This is the reason why the stability criterion for the solid solution under irradiation, when it may be written in a simple analytical form[9,12] implies kinetic parameters together with the thermodynamic characteristics of the system. The above detailed mechanisms, however, are certainly only some particular examples of the various possible mechanisms by which the dissipative processes sustained by irradiation may affect the stability of the solid solutions.

The purpose of this paper is to elucidate under which general conditions the stability of the solid solution may be destroyed by the dissipative processes sustained by irradiation. The method we use is as follows: We define a model solid solution by the atomic concentrations of interstitials, vacancies, and solute atoms, and consider two different regimes for this solution. In the first regime, hereafter referred to as *c* (closed), vacancies and interstitials are simply extra chemical components, with no annihilation reaction allowed (the defect production is stopped once the appropriate point-defect concentrations have been reached). This regime yields the thermodynamical reference state of the solid solution under irradiation. In the second regime, referred to as *o* (open), allowance is made for vacancy-interstitual mutual annihilation. The vacancy and interstitial concentrations of the reference state can only be maintained at the expense of a continuous production of point defects in the system. The question raised is: under what conditions a solid solution which is stable in regime *c* may be unstable in regime *o*. In order to answer this question, we state simple diffusion-reaction equations for the concentration of the various components of the system (Sec. II) and check the stability of the uniform steady-state solution of the above equations with respect to spatial-composition fluctuations of small amplitude (Sec. III). Assuming the uni-

TABLE I. Radiation-induced precipitation in undersaturated binary solid solutions. In complex alloys also, such as stainless steels, unexpected phase changes have been reported. Owing to the poor knowledge of the equilibrium phase diagram outside irradiation it is difficult to certify that the reported precipitation is radiation *induced* rather than accelerated. In the particular case of American Iron and Steel Institute (AISI) 316 stainless steels, however, Brager and Garner (Ref. 34) have checked that the radiation-induced γ' precipitates dissolve outside irradiation at the irradiation temperature.[a]

System	Projectile	Result		Reference
Ni-Be	Ni^+	β-NiBe	heterogenous precipitation at point-defect sinks	Okamoto, Taylor, and Wiedersich (Ref. 27)
Ni-Si	n	γ'-Ni_3Si		Silvestre, Silvent, Regnard, and Sainfort (Ref. 28)
	Ni^+	γ'-Ni_3Si		Barbu and Ardell (Ref. 29)
	e^-	γ'-Ni_3Si		Barbu and Martin (Ref. 30)
Ni-Ge	e^-	γ'-Ni_3Ge		Barbu (Ref. 3)
Al-Zn	n	Zn	Homogeneous precipitation	Farrell (Ref. 31)
	e^-	Zn, GP zones		Cauvin and Martin (Ref. 4)
W-Re	n	χ-WRe_3		Sikka and Motteff (Ref. 32)
	n	χ-WRe_3		Stiegler and Wiffen (Ref. 33)

[a] F. A. Garner (private communication).

form steady state to be stable in regime c, we look for the conditions for the loss of stability in regime o (Sec. IV). The implications of the result are discussed in Sec. V, and specific models of solid solutions under irradiation are briefly analyzed in Sec. VI.

II. THE SOLID-SOLUTION MODEL

For the sake of simplicity, we describe the state of the solid solution under irradiation by the local value of four concentrations: n_A, n_B, n_i, n_v which are, respectively, the solvent, solute, interstitial, and vacancy concentrations (number per lattice site). In fact, a more detailed description might be given by distinguishing the solvent and solute interstitials (and even the mixed interstitials in the case of dumbbell interstitial configuration). However, such refinements would simply make the calculations more complicated without adding much to the point we want to demonstrate.

Assuming that the point-defect concentrations (n_i, n_v) are much smaller than the solute concentration, the total solute concentration n_B is not very different from the concentration of solute on lattice sites. Moreover, assuming lattice sites conservation yields

$$n_A + n_B + n_v \simeq 1 \tag{1a}$$

or

$$n_A + n_B + n_v + n_i \simeq 1\,. \tag{1b}$$

Equation (1a) deals with simple interstitials while (1b) deals with dumbbell interstitials. The balance equations for the three species i, v, B are

$$\frac{\partial n_i}{\partial t} = P - K n_i n_v - div\,\vec{J}_i\,, \tag{2}$$

$$\frac{\partial n_v}{\partial t} = P - K n_i n_v - div\,\vec{J}_v\,, \tag{3}$$

$$\frac{\partial n_B}{\partial t} = -div\,\vec{J}_B\,, \tag{4}$$

where P is the defect production rate, K an effective rate constant for the vacancy-interstitial recombination reaction, n_i, n_v, n_B and $\vec{J}_i$, $\vec{J}_v$, $\vec{J}_B$, respectively, the local concentrations and the fluxes of interstitials, vacancies, and solute atoms. As can be seen from Eqs. (2) and (3) no point-defect elimination on fixed sinks is allowed for, since we assumed the conservation of lattice sites. The model is therefore more appropriate to low-temperature, high-flux irradiation conditions. Relaxing this condition would simply, but prohibitively, increase the number of balance equations. We assume $\vec{J}$ to be zero at the boundary of the system. As explained in the introduction, we consider two different regimes for this system. In regime c interstitials and vacancies are conservative species; K and therefore P must be zero. This does not mean that the vacancy and interstitial concentrations are zero. They are fixed to an arbitrary value, $\bar{n}_i$ and $\bar{n}_v$ and keep this value since no allowance is made for defect production or elimination. In regime o interstitials and vacancies may be eliminated by mutual recombination. The defect production rate P must be adjusted in order to maintain the average defect concentrations at the same level as in regime c:

$$P = K \bar{n}_i \bar{n}_v\,. \tag{5}$$

We now make the assumption that the homogeneous solid solution defined by

$$
\begin{aligned}
&n_i(\vec{r},t)=\bar{n}_i\,,\\
&n_v(\vec{r},t)=\bar{n}_v\,,\\
&n_B(\vec{r},t)=\bar{n}_B
\end{aligned}
\tag{6}
$$

is linearly stable in regime c ($P=K=0$) (for a discussion of stability criteria, see Ref. 20).

In order to check the *linear* stability of a regime, we proceed as follows: We introduce in the system a small amplitude concentration oscillation around $\bar{n}_p$ ($p=i,v,B$):

$$n_p(\vec{r},t)=\bar{n}_p+\nu_p(\vec{k},t)\cos\vec{k}\cdot\vec{r}\,, \tag{7}$$

with $|\vec{k}|=2\pi/\lambda$.

The system is linearly stable if $\nu_p(\vec{k},t)\rightarrow 0$ when $t\rightarrow\infty$ whatever $\vec{k}$. The time evolution of $\nu_p(\vec{k},t)$ is found by introducing (7) in (2)–(4).

In principle, the fluxes $\vec{J}_p$ may be written as a function of the concentration gradients

$$\vec{J}_p=\sum_q c_{pq}\vec{\nabla}n_q\,, \tag{8}$$

where the c_{pq} are functions of the concentrations and possibly of the concentration gradients.[13-15] Since we only discuss the linear stability of the system, (i.e., ν_p small and therefore $\vec{\nabla}n_p$ small) it is sufficient to assume c_{pq} constant when introducing (7) into (2)–(4). Assuming the system isotropic the time evolution of the ν_p's is therefore given by

$$
\begin{aligned}
\frac{\partial\nu_i}{\partial t}&=-k^2c_{ii}\nu_i-k^2c_{iv}\nu_v-k^2c_{iB}\nu_B-K\bar{n}_i\nu_v\\
&\quad-K\bar{n}_v\nu_i\,,\\
\frac{\partial\nu_v}{\partial t}&=-k^2c_{vi}\nu_i-k^2c_{vv}\nu_v-k^2c_{vB}\nu_B-K\bar{n}_i\nu_v\\
&\quad-K\bar{n}_v\nu_i\,,\\
\frac{\partial\nu_B}{\partial t}&=-k^2c_{Bi}\nu_i-k^2c_{Bv}\nu_v-k^2c_{BB}\nu_B\,.
\end{aligned}
\tag{9}
$$

($-k^2c_{ij}$) are the elements of a 3×3 matrix $\underline{c}$. They may in principle be expressed in terms of the mobilities and mutual interaction potentials of the four species A, B, v, i (Refs. 13, 14).

The detailed expression for the elements of the diffusion matrix $\underline{c}$ is beyond the scope of this paper. Explicit examples will be given in Sec. VI. In principle the coefficients c_{pq} may be given the form

$$c_{pq}=\sum_r L_{pr}\frac{\partial\mu_r}{\partial n_q}\,, \tag{10}$$

where L_{pr} are the phenomenological Onsager's coefficients and μ_r the chemical potentials.

Assuming that the system is linearly stable in regime c means that all the eigenvalues of the matrix $\underline{c}$ have negative real part. Similarly, the stability of the system in regime o (P and $K\neq0$) is governed by the sign of the real part of the eigenvalues of the matrix $\underline{o}$ given by:

TABLE II. Alternative notations for the diffusion matrix.

a	b	c
c_{ii}	c_{iv}	c_{iB}
d	e	f
c_{vi}	c_{vv}	c_{vB}
g	h	i
c_{Bi}	c_{Bv}	c_{BB}

$$\underline{o}=\underline{c}+\begin{pmatrix}-K\bar{n}_v & -K\bar{n}_i & 0\\ -K\bar{n}_v & -K\bar{n}_i & 0\\ 0 & 0 & 0\end{pmatrix} \tag{11}$$

or

$$\underline{o}=-k^2\begin{pmatrix}a+K^1\bar{n}_v & b+K^1\bar{n}_i & c\\ d+K^1\bar{n}_v & e+K^1\bar{n}_i & f\\ g & h & i\end{pmatrix}, \tag{12}$$

where

$$K^1=K/k^2\,, \tag{13}$$

and the coefficients a to i are respectively equal to the corresponding elements c_{ii} to c_{BB} of the matrix $\underline{c}$, since the constituents of the system interact through the same potentials and have the same mobilities in the two regimes o and c. In the following we shall use the notations $a,\ldots,i$ or $c_{ii},\ldots,c_{BB}$ without distinguishing between them. Table II gives the correspondence between the two notations.

The question raised in the introduction is: under what conditions at least one of the eigenvalues of the matrix $\underline{o}$ has a positive real part, assuming that all eigenvalues of the matrix $\underline{c}$ have negative real parts. We elucidate this question in the following two sections.

III. FORMULATION OF THE PROBLEM

The general discussion of the sign of the real parts of the eigenvalues of 3×3 matrices is rather tedious. Hints to interesting features, however, have been given by several authors.[16,17] We would rather take advantage of some specific features of our problem which will make the discussion more practicable.

As stated in Sec. II, we want to discuss the sign of the eigenvalues of the matrices $\underline{c}$ and $\underline{o}$. The eigenvalues of $\underline{o}$ are the solution of the characteristic equation

$$\det(\underline{o} - \omega \underline{I}) = 0\,, \tag{14}$$

where $\underline{I}$ is the unit matrix. We recall that

$$\underline{o} \equiv \underline{c} \quad \text{if}\, K = 0\,. \tag{15}$$

Equation (14) may be written as

$$\omega'^3 + a_1 \omega'^2 + a_2 \omega' + a_3 = 0\,, \tag{16}$$

with

$$\omega' = \omega / k^2 \tag{17}$$

and

$$a_1 = a + e + i + K^1(\bar{n}_i + \bar{n}_v)\,, \tag{18}$$

$$a_2 = ae + ei + ia - hf - cg - bd + K^1[\bar{n}_i(a + i - d) + \bar{n}_v(e + i - b)]\,, \tag{19}$$

$$a_3 = aei - ahf - cge + bgf + cdh - bdi + K^1[\bar{n}_i(ai + gf - di - cg) + \bar{n}_v(ei + ch - hf - bi)]\,. \tag{20}$$

According to the Routh-Hurwitz criterion,[18] Eq. (16) has three solutions with negative real parts if and only if

$$a_1 > 0\,, \tag{21}$$

$$a_1 a_2 - a_3 > 0\,, \tag{22}$$

$$a_3 > 0\,. \tag{23}$$

The question raised in the introduction is: under what conditions at least one of the inequalities (21)–(23) is violated for $K^1 \neq 0$ (o unstable) knowing that all are fulfilled for $K^1 = 0$ (c stable). We were unable to give the answer to this question in a synthetic form. However, without much loss of generality, the following two assumptions greatly simplify the discussion:

(A_1) $b = d = 0$ or $c_{iv} = c_{vi} = 0$,

(A_2) $\bar{n}_i = \bar{n}_v = (P/K)^{1/2}$.

Assumption (A_1) is indeed verified by the specific models of solid solutions under irradiation which are discussed in Sec. VI. Indeed, no coupling exists between the interstitial and vacancy fluxes as long as the range of the interaction potentials between the constituents does not exceed the mutual recombination radius of the Frenkel pair. That this is the case is certainly a good approximation. Assumption (A_2) simplifies the analytical treatment but may be relaxed for numerical applications of the method.

With assumptions (A_1) and (A_2), the conditions (21) to (23) write:

$$a + e + i + K_1 > 0\,, \tag{24}$$

$$a^2(e + i) + e^2(i + a) + i^2(a + e) + 2aei - cg(a + i) - hf(e + i) + K_2 > 0\,, \tag{25}$$

$$aei - ahf - cge + K_3 > 0\,, \tag{26}$$

with

$$K_1 = 2\sqrt{KP}/k^2\,, \tag{27}$$

$$K_2 = \frac{\sqrt{KP}}{k^2}\left(2(a + e + i)^2 - (a^2 + e^2) - (c + f)(h + g) + \frac{2\sqrt{KP}}{k^2}(a + e + 2i)\right)\,, \tag{28}$$

$$K_3 = \sqrt{KP}\,[i(a + e) + (h - g)(c - f)]/k^2\,. \tag{29}$$

The statement that regime c is stable implies that the conditions (24)–(26) are fulfilled when $K_1 = K_2 = K_3 = 0$. Assuming this is the case, what are the requirements for at least one of these conditions to be violated when $KP \neq 0$?

The following section gives a detailed discussion of these requirements. Before turning to this section we introduce the following useful change in variables:

$$\begin{aligned} c &= S(c)\frac{G}{v}\,, \\ g &= S(g)Gv\,, \\ f &= S(f)\frac{F}{u}\,, \\ h &= S(h)Fu\,, \\ S(x) &= \operatorname{sgn}(x)\,, \end{aligned} \tag{30}$$

where F, G, u, v are positive numbers.

Moreover, we simplify the discussion by making assumption (A_3): the diagonal diffusion coefficients (c_{ii}, c_{vv}, c_{BB}) are all positive. This is a sufficient condition for (24) to be valid. This condition is valid for the specific models which we will study in Sec. VI.

IV. CONDITION FOR DESTABILIZATION BY DISSIPATIVE PROCESSES

We first notice that according to assumption (A_3) and to expression (27) of K_1, condition (24) is always fulfilled whatever the values of K and P. Therefore the loss of stability can only result from the violation of at least one of the two inequalities (25) and (26).

The latter inequalities, can be written with the help of variables defined by (30) as

$$A - S(cg)(a + i)G^2 - S(hf)(e + i)F^2 + K_2 > 0\,, \tag{31}$$

with

$$A=a^2(e+i)+i^2(a+e)+e^2(a+i)+2aei \qquad (32)$$

and

$$aei-S(hf)aF^2-S(cg)eG^2+K_3>0\,. \qquad (33)$$

The discussion can be easily carried out in the F-G plane. When $K_2=K_3=0$ (regime c), the relations (31)–(33) are fulfilled in a portion of the first quadrant of the F-G plane bordered by the conic section of the equation which is obtained by setting the left-hand side of Eqs. (31) and (33) equal to zero.

For example, the equation of the conic section corresponding to Eq. (33) is

$$aei-S(hf)aF^2-S(cg)eG^2=0\,. \qquad (34)$$

It is straightforward to verify that whatever the combination of the signs which are attributed to c, f, g, h, condition (33) is more restrictive than (31). As a consequence a sufficient condition for destabilization is that condition (33) is violated when $K_3\neq 0$.

When $K_3\neq 0$ the necessary condition for (33) to be violated [knowing (33) is fulfilled when $K_3=0$] is

$$K_3<0\,.$$

Introducing (30) into (29) gives

$$K_3=\frac{\sqrt{KP}}{k^2}\left[i(a+e)+FG\left(S(hc)\frac{u}{v}+S(fg)\frac{v}{u}\right)-S(hf)F^2-S(cg)G^2\right]<0\,, \qquad (35)$$

which again is fulfilled in a portion of the F-G plane limited by the conic section

$$S(hf)F^2+S(cg)G^2-FG\left(S(hc)\frac{u}{v}+S(fg)\frac{v}{u}\right)-i(a+e)=0\,. \qquad (36)$$

In summary, we were looking for the conditions under which the system being stable in regime c may become unstable in regime o. A sufficient condition for this to be *possible* is that the two following inequalities are fulfilled simultaneously:

$$aei-S(hf)aF^2-S(cg)eG^2>0\,, \qquad (37)$$

$$S(hf)F^2+S(cg)G^2-FG\left(S(hc)\frac{u}{v}+S(fg)\frac{v}{u}\right)-i(a+e)>0\,. \qquad (38)$$

Once these two conditions are fulfilled, the condition for regime o to be effectively unstable is provided by the violation of inequality (33), namely

$$\frac{\sqrt{KP}}{k^2}>\frac{aei-S(hf)aF^2-S(cg)eG^2}{S(hf)F^2+S(cg)G^2-FG\left(S(hc)\frac{u}{v}+S(fg)\frac{v}{u}\right)-i(a+e)}\,. \qquad (39)$$

We now discuss the conditions under which Eqs. (37) and (38) are fulfilled simultaneously. We first notice that the nature of the conic sections which delineate the portion of the F-G plane where the above conditions are fulfilled only depends on the sign of hf, cg, hc, fg and not on the signs of h, f, c, g individually. Table III summarizes all the possible situations: they reduce to eight. Table III also shows the portions of the F-G plane positive quadrant where conditions (37) and (38) are respectively fulfilled, and finally the conditions under which these portions overlap (unhatched domains).

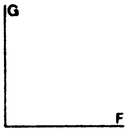
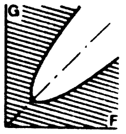
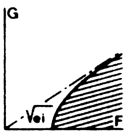
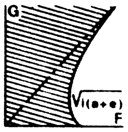
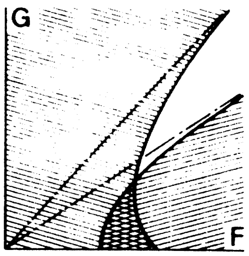
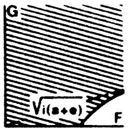
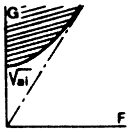
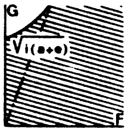
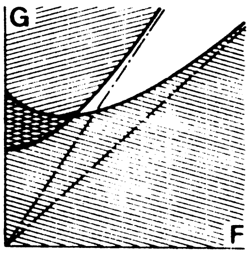
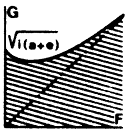
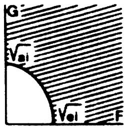
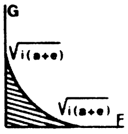
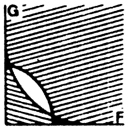
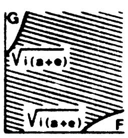
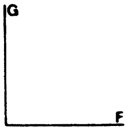
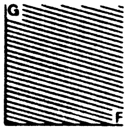
Simple inspection of Table III reveals the following features:

(a) If regime c is to be destabilized by dissipative processes, this can only result from the nondiagonal terms of the matrix $\underline{c}$. This point was already suggested by Ref. 17. The physical meaning of this is that the cross interactions between the species (e.g., solute-point-defect interaction) and the coupling coefficients between the fluxes (e.g., the solute drag by point-defect fluxes) play the key role in the destabilization process. That point-defect fluxes may develop under irradiation even in the absence of point-defect sinks, as in our model system, results from the point-defect mutual recombination as shown in Ref. 4. Such fluxes can therefore only appear in regime o.

(b) The conditions for the destabilization of c to be *possible* are very loose indeed. The only cases where the destabilization is *not possible* are (cf. lines 7 and 8 of Table III) when c_{vB} and c_{Bi} on one hand and c_{iB} and c_{Bv} on the other have the same sign in pairs. In all other cases, it is possible to find a set of values for the parameters which will make it possible for the system to be stable in regime c and unstable in regime o. Assuming that the parameters have appropriate values, the sufficient condition for the regime o to be unstable is given by the relation (39). Usually, the parameters a to i have a term of zeroth order in k^2,[13,15] so that, except for a fortuitous cancellation of this term in the dominator of the right-hand side of Eq. (39) it will always be fulfilled for sufficiently small values of k^2.

Table III therefore gives the conditions for the system to be unstable in regime o. We discuss

TABLE III. Regions of dissipative instability (unhatched) in the parameter space.

f	h	c	g	hf	cg	hc	fg	DOMAIN OF VALIDITY OF CONDITION 37	 CONDITION 38	DOMAIN OF COMPATIBILITY OF 37 AND 38 Shape and location	 Condition of existence
+ -	- +	+ -	- +	-	-	-	-			Same as the domain of validity of 39	No extra Condition
+ -	+ -	+ -	- +	+	-	+	-				$\frac{e}{a} < \sqrt{\frac{-fg}{ch}}$
+ -	+ -	- +	+ -	+	-	-	+				
+ -	- +	- +	- +	-	+	+	-				
+ -	- +	+ -	+ -	-	+	-	+				
+ -	+ -	- +	- +	+	-	-	-				hc ≠ fg
+ -	- +	- +	+ -	-	-	-	-			Conditions 37 and 38 are not compatible	
+ -	+ -	+ -	+ -	+	+	+	+				

this question in more detail in the following section.

V. DISCUSSION

A. Stability criterion for a solid solution under irradiation

We have just demonstrated that it is possible for a homogeneous solid solution containing vacancies and interstitials to be stable when vacancies and interstitials are conservative species and unstable when vacancy-interstitial mutual recombination is allowed for. The required conditions on the parameters of the system are summarized in Table III.

This justifies the idea stated in the Introduction that the stability of a solid solution under irradiation is not governed only by the properties of the free energy of the system, as a function of the point-defect concentrations. Indeed, the state of a system governed by Eqs. (2)-(4) and (8) is entirely defined once the temperature T and the concentrations $\bar{n}_B$, $\bar{n}_v$, $\bar{n}_i$ are given. In the present model, the point-defect concentrations ($\bar{n}_v$, $\bar{n}_i$) are uniquely defined by the temperature (which fixes K) and the irradiation flux (which fixes P); according to assumption (A_2) in Sec. III

$$\bar{n}_1 = \bar{n}_v = \left(\frac{P}{K}\right)^{1/2} .$$

Therefore, the domain of radiation-induced instability can be defined in a flux-temperature-concentration diagram.

Such a diagram has already been used to represent the experimental limit of solubility of Si in Ni under irradiation.[2] In this latter case however, this representation is only tentative. Indeed, from theoretical arguments it is shown that the solubility limit under irradiation in this Ni-Si system is a function of the dislocation density[12] and it is not certain that the dislocation density under irradiation is independent of the history of the system. It has sometimes been objected that the irradiation flux is *not* a thermodynamic *intensive* variable (since there is no associated extensive variable), and should therefore not be confused with variables such as the temperature or the composition.[1] This is perfectly correct. Nevertheless, the flux-temperature-composition diagram is simply the diagram of the control parameters of the state of the solid solution under irradiation. When the irradiation flux is zero, the control parameters reduce to the standard thermodynamic variables. This is an illustration of a common feature of the theory of dissipative structures.[19]

According to the preceding sections, radiation-induced solid-solution instability may have its origin in two different processes:

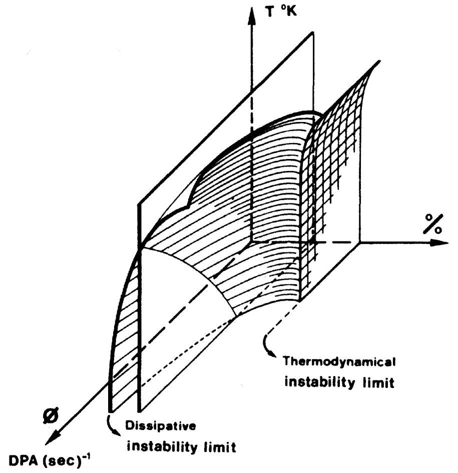


FIG. 1. Tentative representation of the instability limit of a solid solution under irradiation.

(a) Either the diffusion coefficients c_{ij} are such that the system is unstable in regime c. This corresponds to the case where the solid solution supersaturated with point defects is unstable for thermodynamic reasons;

(b) or the coefficients c_{ij} are such that the system is stable in regime c but unstable in regime o. The instability is driven by the dissipative processes.[20]

Following a general argument of the theory of dissipative structure,[19,20] we suggest that for *a given temperature* when the point-defect supersaturation is low (i.e., when the irradiation flux is small), the minimum solute content for the solid solution to be unstable is determined by criterion (a). In other words, the stability criterion may be deduced from the thermodynamics of the system. On the other hand, when the point-defect supersaturation is large (and therefore the dissipation is intense) criterion (b) will hold. Figure 1 depicts a possible shape for the stability limit in the flux-temperature-composition space.

B. The time scale for the dissipative instability

Once the system is known to be unstable in regime o, it is unstable only for those harmonics of the concentration fluctuations with a wave length ($2\pi/k$) larger than a threshold value given by Eq. (39) which can also be written

$$\lambda^2 > \lambda^{*2} = \frac{4\pi^2}{\sqrt{KP}} \, \frac{aei - S(hf)aF^2 - S(cg)eG^2}{S(hf)F^2 + S(cg)G^2 - FG\left(S(hc)\,\dfrac{u}{v} + S(fg)\,\dfrac{v}{u}\right) - i\,(a+e)} . \tag{40}$$

λ^* may be taken as a scaling length of the system. We define $k^* = 2\pi/\lambda^*$.

For a given set of diffusion coefficients c_{ij} [which implies a given value of the average defect concentration $\bar{n}_d = \bar{n}_i = \bar{n}_v = (P/K)^{1/2}$] Eq. (40) shows that $k^2/\sqrt{KP}$ fixes the magnitude of the reduced wave vector k/k^*. On the other hand, as shown by Eqs. (17) and (27)–(29), $\omega' = \omega/k^2$ is fixed once

c_{ij}, $\bar{n}_d$, and $k^2/\sqrt{KP}$ are given. The latter parameter may be rewritten as $k^2\bar{n}_d/P$ which shows that $1/P$ appears as a scaling time.

Indeed, for given diffusion coefficients point-defect concentrations (P/K) and reduced wavelength $(\propto k^2\bar{n}_d/P)$ increasing the defect production rate increases k^2 accordingly, and ω as shown by Eq. (17). In other words, with the constraints just cited the relaxation time of a fluctuation $(1/\omega)$ is proportional to $1/P$. Therefore, the more dissipative the system in regime *o*, i.e., the larger the defect production rate necessary to sustain a given defect supersaturation, the shorter the relaxation times of the concentration fluctuations, and in particular the more rapid the radiation-induced precipitation process.

C. Comparison with previous work

In a previous attempt to describe radiation-induced destabilization[21] the author had restricted himself to a three-components system (A, i, v). The instability which was discussed was that of the homogeneous point-defect population. The loss of stability in this earlier work resulted from the change of sign of one of the *diagonal* terms of the matrix $\underline{c}$.

The required change of sign was triggered by an attractive defect-defect interaction energy which could drive up-hill diffusion. In such a model, the instability had a thermodynamic origin, while the vacancy-interstitial mutual recombination reaction had a stabilizing effect as was discussed in the original paper.[21] Indeed, when the point-defect concentration increases locally, the mutual recombination increases and therefore opposes the growth of the concentration fluctuation.

In the present study, however, this is no longer true as was just shown in the preceding sections. Interstitial-vacancy recombination may trigger the instability. One possible mechanism for this to occur has been proposed in Ref. 4. If a solute concentration heterogeneity attracts the point defects, the recombination rate will be larger in the region of this heterogeneity, therefore sustaining a point-defect current towards this region. The defect current may drift a solute current which, depending on the sign of the latter, enhances or smooths the solute concentration heterogeneity. We now turn to specific solid solution models.

VI. APPLICATION TO SPECIFIC MODELS

Several models are available for the description of a solid solution under irradiation. They have been used until now to describe radiation-induced segregation at point-defect sinks, either in dilute alloys[22,3] or in concentrated alloys.[23] In this section we show that the solid solutions obeying these models may become unstable under irradiation.

TABLE IV. Sign of the diffusion coefficients in the dilute-solid-solution models of Refs. 22,3.

c_{pq}	i	v	B
i	+	0	±
v	0	+	±
B	+	±	+

For all the above models, the balance equations for the interstitials, vacancies, and component B are given by Eqs. (2)–(4). Moreover, assumptions (A_1) and (A_3) of Sec. III are fulfilled, i.e.,

$$(A_1)\quad c_{iv}=c_{vi}=0\,,$$

$$(A_3)\quad c_{ii}>0,\quad c_{vv}>0,\quad c_{BB}>0\,.$$

The expressions for the remaining coefficients vary from model to model.

(a) *Dilute solid solutions*: The statistical thermodynamical model of dilute solid solutions containing point defects proposed by Howard and Lidiard[24] has been extended to the case where non-interacting vacancies and interstitials are simultaneously present.[3,22,25] The two versions of this extension simply differ by the expressions of c_{pq} in terms of the jump frequencies of the defects in the vicinity of the solute atoms.

The sign rules obeyed by c_{pq} according to Barbu[25] are depicted in Table IV. Comparison of Tables III and IV shows that the stability of such a solid solution under irradiation is not guaranteed. Indeed, relaxing assumption (A_2) we have verified by numerical evaluation of Eqs. (21)-(23) that some steady states predicted by Barbu's model are indeed unstable, in particular at low temperature. It is worth noticing that it is precisely in the region of the control parameter space where the algorithm used to solve numerically Johnson and Lam[22] equations often fails to converge.

(b) *Concentrated solid solutions*: The description by Manning of diffusion in concentrated alloys under irradiation[26] has been simplified by Wiedersich, Okamoto and Lam[23]. Simple inspection

TABLE V. Sign of the diffusion coefficients in the concentrated solid-solution model of Ref. 23.

c_{pq}	i	v	B
i	+	0	±
v	0	+	±
B	+	−	+

of the balance equations of this latter model shows the sign rules depicted in Table V. According to Table III, radiation induced loss of stability is possible in this model, except for $c_{iB} < 0$ and $c_{vB} > 0$.

The above two models are only approximate models of the thermodynamics of a solid solution containing interstitials and vacancies. A general model is highly desirable.

VII. SUMMARY AND CONCLUSION

The vacancy-interstitial mutual recombination reaction is shown to play a crucial role in the stability of a binary solid solution under irradiation. For given point-defect concentration, the solid solution may be unstable if this reaction is allowed for, while it is linearly stable if this reaction is forbidden.

Under simplifying assumptions which are shown not to be very restrictive, the general conditions for the above behavior have been elucidated and are depicted in Table III. Available models for solid solutions under irradiation may exhibit the predicted loss of stability.

Although this was not done in detail in the above sections, the formalism used suggests that the reverse process may occur. An unstable solid solution might be stabilized under irradiation by the vacancy-interstitial recombination reaction. Finally, according to the above arguments radiation-*induced* precipitation might provide an example for the formation of dissipative structures in solids.

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[1] K. C. Russell, *Radiation effects in Breeder Reactor Structural Materials*, edited by M. L. Bleiberg *et al.* (AIME, New York, 1977), p. 821.

[2] G. Martin, J. L. Bocquet, A. Barbu, and Y. Adda, cf. Ref. 1, p. 899.

[3] A. Barbu, thesis, University of Nancy, France, 1978 (unpublished); Rapport No. CEA-R-4936, Gif-sur-Yvette, France, 1979 (unpublished).

[4] R. Cauvin and G. Martin, J. Nucl. Mater. 83, 67 (1979).

[5] Y. Adda, M. Beyeler, and G. Brebec, Thin Solid Films 25, 107 (1975).

[6] J. L. Bocquet and G. Martin, J. Nucl. Mater. 83, 186 (1979).

[7] L. Kaufman, J. S. Watkins, J. H. Gittus, and A. P. Miodownik, Calphad J. 1, 281 (1977).

[8] K. C. Russell, J. Nucl. Mater. 83, 176 (1979).

[9] S. I. Maydet and K. C. Russell, J. Nucl. Mater. 64, 101 (1977).

[10] M. R. Mruzik and K. C. Russell, J. Nucl. Mater. 78, 343 (1978).

[11] H. Wiedersich, P. R. Okamoto, and Nghi Q. Lam, cf. Ref. 1, p. 801.

[12] G. Martin, Philos. Mag. A38, 131 (1978).

[13] D. De Fontaine, J. Phys. Chem. Solids 33, 297 (1972).

[14] D. De Fontaine, J. Phys. Chem. Solids 34, 1285 (1973).

[15] J. E. Morral and J. W. Cahn, Acta Metall. 19, 1037 (1971).

[16] H. G. Othmer and L. E. Scriven, Ind. Eng. Chem. 8, 302 (1969).

[17] J. J. Tyson and J. C. Light, J. Chem. Phys. 59, 4164 (1973).

[18] F. R. Gantmacher, *Théories des Matrices* (Dunod, Paris, 1966), Vol. 2, p. 191.

[19] P. Glansdorff and I. Prigogine, *Structure, Stabilité et Fluctuations* (Masson, Paris, 1971).

[20] G. Nicolis and I. Prigogine, *Self Organization in Non Equilibrium Systems* (Wiley, New York, 1977), p. 70.

[21] G. Martin, Philos. Mag. 32, 615 (1975).

[22] R. A. Johnson and Nghi Q. Lam, Phys. Rev. B 13, 4364 (1976).

[23] H. Wiedersich, P. R. Okamoto, and Nghi Q. Lam, J. Nucl. Mater. 83, 98 (1979).

[24] R. E. Howard and A. B. Lidiard, Rep. Prog. Phys. 27, 161 (1964).

[25] A. Barbu, Acta Met. (to be published).

[26] J. R. Manning, Bull. Am. Phys. Soc. 23, 287 (1978).

[27] P. R. Okamoto, A. Taylor, and H. Wiedersich, *Fundamental Aspects of Radiation Damage in Metals*, edited by M. T. Robinson *et al.*, USERDA Conference 751006 (1975), p. 1188.

[28] G. Silvestre, A. Silvent, C. Regnard, and G. Sainfort, J. Nucl. Mater. 57, 125 (1975).

[29] A. Barbu and A. J. Ardell, Scripta Metall. 9, 1233 (1975).

[30] A. Barbu and G. Martin, Scripta Metall. 11, 771 (1977).

[31] K. Farrell (private cummunication).

[32] V. K. Sikka and J. Moteff, Metall. Trans. 5, 1514 (1974).

[33] J. O. Stiegler and F. W. Wiffen, Report No. ORNL-TM-4500 (1974), p. 52.

[34] H. R. Brager and F. A. Garner, J. Nucl. Mater. 73, 9 (1978).