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## 1. Introduction

Experiments have shown that under irradiation precipitates may either grow or shrink, that equilibrium phases may dissolve and be replaced with non-equilibrium phases and that precipitation sequences may be altered. The situation is evidently very complex and several different mechanisms are operating to modify microstructural phase stability under irradiation.

The mechanisms that have been proposed and in some cases demonstrated, can be classified.

a) Radiation Enhanced Diffusion. The increase in point defect population caused by atomic displacements causes an increase in diffusion rates.<sup>(1)</sup> This often permits sluggish phase transformations to proceed to completion under irradiation when thermal reaction had apparently ceased.

b) Radiation Induced Segregation.<sup>(2)</sup> During irradiation large numbers of point defects are generated, diffuse to sinks and annihilate. Any coupling between solute atoms and this flux of defects will induce a flux of solute towards or away from the sinks. The segregation induced by the solute flux can cause the composition of local regions to cross the phase boundary so that precipitation can occur.<sup>(3)</sup> Elsewhere in the matrix a corresponding depletion of solute can cause precipitate dissolution.

c) Other Flux Coupling Phenomena. A coupling between defect fluxes and solute atoms may occur near precipitates to aid the defect annihilation. For example,<sup>(4)</sup> an incoherent precipitate may annihilate vacancies at its surface only if the resultant volume strain is relieved by transfer of solute into or out of the precipitate (depending on the relative solute - atom sizes in the matrix and precipitate). Alternatively Martin<sup>(5)</sup> has proposed that solute concentration fluctuations may attract defects and enhance recombination. The resultant depletion of defects induces a further defect flux into

the region and this may drag more solute and enhance the intensity of the fluctuation to the point where precipitation can occur.

d) Cascade and Displacement Effects. The damage process may directly affect precipitates by removing solute atoms from a precipitate by energetic knock-on or by cascade dissolution at the surface of a precipitate.<sup>(6,7)</sup>

e) Defect Concentration Effects. In contrast to the effect of defect fluxes which is involved in a), b) and c), it has been proposed<sup>(8)</sup> that the steady-state defect concentration under irradiation may itself destabilize a phase and permit an alternative phase to precipitate instead.

This paper represents a new approach to mechanism e). The steady-state defect concentrations under irradiation are generally too small to produce the ~ 10-100 kJ/mol in internal energy required to destabilize equilibrium phases.

However, in ordered alloys in addition to vacancy and interstitial defects caused by atom displacements, there are anti-structure atoms caused by atom replacements. Since the replacements often exceed the displacements by between one and two orders of magnitude the steady-state concentration of anti-structure atoms can be much larger than for other defects. If the ordered phase has a high ordering energy and a slow reordering rate, the energy involved in radiation-induced disordering can easily reach the levels required to modify phase stability.

In this paper we propose a detailed model for the disordering of phases by irradiation and the calculation of radiation modified phase diagrams.

## 2. Radiation Induced Disorder

There is abundant evidence that radiation induces disorder.<sup>(9-12)</sup>

An irradiation process which creates atomic displacements will also create replacements. In an ordered alloy both events produce point defects; displacements producing frenkel pairs and replacements producing anti-structure atoms. Since these events are caused by the incident particles with energies much greater than the thermal energy per atom, the defect production itself is independent of temperature (except for any temperature induced defocussing of collision sequences).

Any disordered alloy will return to its equilibrium degree of order provided the appropriate diffusion process can operate. The radiation-produced vacancies and interstitials enhance diffusion (provided that they are mobile) so that radiation can also enhance the reversion to the equilibrium degree of order.

In an ordered alloy under irradiation we therefore have two opposing processes continuing, a disordering and a reordering, with some steady-state degree of order being established when the two rates balance. The purpose of this section is to describe a simple model for calculating this steady-state order. We consider only long range order of stoichiometric ordered phases.

The Bragg-Williams definition of the long range order parameter for a binary alloy with atoms arranged on two sub-lattices  $\alpha$  and  $\beta$  is

$$S = \frac{f_{A\alpha} - X_A}{1 - X_A} \quad (1)$$

where  $f_{A\alpha}$  is the probability of an A atom being at an  $\alpha$  lattice site, and  $X_A$  is the atomic fraction of A atoms.  $S=1$  when the alloy is completely ordered and  $S=0$  when it is completely random. When the ordered alloy is irradiated, a rate equation can be written for the balance between the disordering and reordering rates

$$\frac{dS}{dt} = \left(\frac{dS}{dt}\right)_{Irr} + \left(\frac{dS}{dt}\right)_{Th} \cdot \quad (2)$$

The second term on the right-hand side is the irradiation enhanced thermal reordering rate.

The solution of this steady-state equation gives the steady-state degree of order under irradiation. In order to find this we must first express the ordering and disordering rates in terms of the irradiation and material parameters and to this we now turn.

### 2.1. Irradiation Disordering

The unit of radiation damage, displacement per atom (dpa), which has

been commonly used for void swelling studies, is not appropriate for radiation induced disorder. We need instead the total number of atoms replaced by other atoms during irradiation. A replacement event can be either a direct replacement or the production of an interstitial which recombines with a vacancy or migrates to a defect sink. If we assume that atoms are randomly replaced by other atoms, it can be easily shown by probability considerations that

$$\left(\frac{dS}{dt}\right)_{\text{Irr}} = - \left(\frac{\nu_r}{\nu_d}\right) kS \quad (3)$$

where  $k$  is the dpa rate,  $\nu_r$  is the number of replacements and  $\nu_d$  is the number of displacements.

There are different mechanisms by which an ordered alloy can be disordered by irradiation. In the case of disordering due to focused replacement sequences (or dynamic crowdions), disordering depends on crystallographic directions and equation (3) should be multiplied by a geometric factor. Disordering can occur locally in displacement spikes by uncorrelated recombinations of frenkel pairs or by formation of defect clusters (vacancy loops formed by cascade collapse for example). The mixing of atoms in these regions is probably random and can, therefore, be approximated by equation (3). In general, we introduce a disordering efficiency  $\epsilon$  and write

$$\left(\frac{dS}{dt}\right)_{\text{Irr}} = - \epsilon kS \quad (4)$$



The parameter  $\epsilon$  is of the order of the ratio  $(\nu_r/\nu_d)$ , which depends on the structure of displacement cascade or the types of irradiation. Under neutron or heavy-ion irradiation conditions,  $\epsilon$  could vary from approximately 10 to 100<sup>(33)</sup>. While under electron irradiation,  $\epsilon$  is approximately 1 ~ 3.

## 2.2. Irradiation Enhanced Thermal Reordering

Nowick and Weisberg<sup>(13)</sup> consider an order-disorder transition as a chemical reaction in which a pair of A-B atoms at the wrong lattice sites is interchanged to give an A-B pair at the right lattice sites.



The rate constants for the reaction are given by

$$k_1 = \nu_1 \exp(-U/k_B T) \quad (5b)$$

$$k_2 = \nu_2 \exp[-(U+V)/k_B T] \quad (5c)$$

where  $U$  is the energy barrier for the reaction and the activation energy  $V$  is the energy reduction when a wrong A-B pair transforms into a right A-B pair.  $V$  depends on the instantaneous configuration of atoms (or the degree of order),  $\nu_1$  and  $\nu_2$  are frequency factors.

Nowick, et al.<sup>(13)</sup> show that at low temperatures where  $S$  approaches unity the solution of the chemical rate equation reduces to

$$\frac{1-S}{1-S_e} = \coth(xt+y) \quad (6a)$$

where  $S_e$  is the equilibrium order parameter,  $y$  is a constant.

For our purpose we require the time derivative of S,

$$\left(\frac{dS}{dt}\right)_{th} = \frac{x(1-S)^2}{(1-S_e)} - (1 - S_e)x \quad (6b)$$

with the rate constant x in the absence of irradiation being <sup>(13)</sup>

$$x = (\nu_r \nu_w)^{1/2} \left[\frac{x_A}{x_B}\right]^{1/2} Z_\beta \exp [-(U+V_0/2)/k_B T] \quad (7)$$

where  $V_0$  is the activation energy when  $S=1$ .  $Z_\beta$  is the number of  $\beta$  sites which are nearest neighbors to an  $\alpha$  site while  $\nu_r$  and  $\nu_w$  are the frequency factors for a right and a wrong pair, respectively. If the activation entropy is neglected, these frequencies are close to the Debye frequency. Although equation (6a) is derived for S close to one, it has been shown to fit experimental data from  $Cu_3Au$  and  $Ni_3Mn$  quite well for the whole range of order. <sup>(13-17)</sup> This has been justified by Nowick et al., <sup>(13)</sup> in a detailed mathematical argument in which the theoretical prediction gave a satisfactory fit up to 30°C from the critical temperature. In systems where the order parameter is close to unity up to the transition temperature (eg.  $Cu_3Au$ ) or for ordered compounds as discussed later in this paper, the model is at its best.

The mass reaction model described above, however, does not relate the kinetics of order-disorder transition to the point defects. To modify the model for alloys under irradiation, one simply considers vacancies and interstitials as species of catalyst for the chemical reaction in equation (5a).

Consider first the vacancy mechanism; there are different paths for the order-disorder reaction of an A-B pair. Figure 1 shows the most probable

path which consists of two successive jumps of the A and B atoms involving only one vacancy. By this reaction path, the Boltzmann factor with the energy barrier  $U$  can be written as

$$\exp(-U_V/k_B T) = C_V \exp(-E_{V0}^m/k_B T) (Z_\alpha + Z_\beta - 2) \quad (8)$$

where  $C_V$  is the concentration of vacancies and  $E_{V0}^m$  is the vacancy migration energy for those vacancy jumps which cause the re-ordering (this need not be identical to  $E_V^m$  for the non-ordering jumps in the alloy).

Transition from a wrong A-B pair to a right A-B pair by this reaction path can begin with a vacancy either at one of the  $Z_\alpha$  sites around a  $\beta$  type vacancy or at one of the  $Z_\beta$  sites around an  $\alpha$  vacancy. The total number of such reaction paths for the A-B pair considered, is therefore,  $(Z_\alpha + Z_\beta - 2)$ . In both CsCl and AuCu<sub>3</sub> type superlattices,  $Z_\alpha + Z_\beta - 2 = 14$ .

The pre-exponential factor for a reaction path of non-successive jumps involving two vacancies is  $(C_V)^2$ . This and other less probable paths are, therefore, negligible compared to the most probable path of two successive jumps involving only one vacancy.

Order-disorder by an interstitialcy mechanism is less understood because of the more complicated interstitial migration process. Experimental evidence<sup>(18-20)</sup> and theoretical calculations<sup>(21,22)</sup> show that interstitials in pure metals (Al, Cu, Ni, Mo, Fe) are in the configuration of  $\langle 100 \rangle$  dumbbells for fcc and  $\langle 110 \rangle$  dumbbells for the bcc structure. These self-interstitials migrate by combined rotational and translational jumps as shown in Figure 2.<sup>(23)</sup> In such cases an A-B pair on the wrong sites can be transferred to right sites by three successive jumps involving one dumbbell. This dumbbell must contain the appropriate atom necessary to give a right atom in its final jump. An example in fcc is shown in Figure 3. Other

reactions for the A-B pair involving more than one interstitial can be neglected compared to the most probable path involving only one interstitial.

However, migration of dumbbell interstitials may be different in alloys. When there is a large difference between the effective atomic volumes of the alloying elements the undersized atoms are preferentially accommodated at the dumbbells. As a result only the undersized atoms are diffusing by this mechanism and the order-disorder reaction is little affected. In general, each reaction path containing three successive jumps should be weighted by a geometric factor and a size dependent probability factor. While the kinetics of order-disorder transition by the interstitialcy mechanism is still under study, we can introduce an interstitialcy re-ordering efficiency,  $\sigma$ , and express the Boltzmann factor with the energy barrier  $U$  in equation (8) as:

$$\exp(-U_i/k_B T) = \sigma C_i \exp(-E_{i0}^m/k_B T) \quad (9)$$

where  $C_i$  is the concentration of the interstitials and  $E_{i0}^m$  is an effective (ordering) migration energy of the dumbbell. The parameter  $\sigma$  contains geometric factors determined by the numbers of the reaction paths and the probability factors for reactions to take place by these paths.

By combining equations (8) and (9), equation (7) can be rewritten as

$$x = \{v_v C_v \exp(-E_{v0}^m/k_B T)(Z_\alpha + Z_\beta - 2) + v_i \sigma C_i \exp(-E_{i0}^m/k_B T)\} \left[\frac{x_A}{x_B}\right]^{1/2} Z_\beta \exp(-V_0/2k_B T) \quad (10)$$

where

$$2v_v = (v_r v_w)_v^{1/2}$$

$$3v_i = (v_r v_w)_i^{1/2}$$

$$V_0 = \begin{cases} -14\Omega & \text{for bcc} \\ -6\Omega & \text{for fcc} \end{cases} \text{ using the quasi-chemical model for the} \\ \text{ordering energy } \Omega = V_{AB} - \frac{V_{AA} + V_{BB}}{2} .$$

The factors two and three in these frequencies reflect the fact that a single pair inversion requires two vacancy jumps or three interstitial jumps.

By inserting  $x$  from equation (10) into equation (6b) the radiation enhanced ordering rate can now be determined in terms of the material parameters.

The steady state defect concentrations ( $C_V$  and  $C_i$ ) can be calculated, following Brailsford and Bullough,<sup>(24)</sup> by solving the steady state rate equations:

$$\frac{\partial C_i}{\partial t} = k - D_i C_i k_i^2 - \alpha C_i C_V = 0$$

$$\frac{\partial C_V}{\partial t} = k' - D_V C_V k_V^2 - \alpha C_i C_V = 0$$

where  $\alpha$  is a defect recombination parameter;  $k_i^2$  and  $k_V^2$  are the effective sink strengths for the interstitials and the vacancies respectively in the crystal under irradiation. Appropriate sink strengths can be used depending on the types of defect sinks present under different irradiation parameters. For simplicity we consider a stable radiation induced dislocation network to be the major sink and express the sink strengths as a function of the dislocation density  $\rho_d$ ,

$$k_i^2 = Z_i \rho_d$$

$$k_V^2 = Z_V \rho_d$$

The bias factors  $Z_i$  and  $Z_V$  given by Brailsford and Bullough are close to unity and differ by a few percent.

### 2.3. The Order-Disorder Transformation Under Irradiation

Having obtained both the ordering and disordering rates from the previous sections we can now determine the steady-state order by inserting them in the rate equation (2).

The general solution to this rate equation with an initial condition  $S = S_0$  at  $t = 0$  is

$$S(t) = 1 - p + \frac{p-q}{1 - \left(\frac{S_0+q-1}{S_0+p-1}\right) \exp(zt)} \quad (11a)$$

where  $z = \{\epsilon^2 k^2 + 4x[x + \epsilon k/(1 - S_e)]\}^{1/2}$ ,

$$p = (-\epsilon k + z)(1 - S_e)/(2x),$$

$$q = (-\epsilon k - z)(1 - S_e)/(2x),$$

$S_e$  is the equilibrium long range order parameter and  $x$  the reaction constant to be determined. We intend to comment on this time variation of order under irradiation in a later paper; here we concentrate on the steady state solution when equation (2) is set equal to zero and  $t \rightarrow \infty$  in equation (11a).

This gives

$$S = 1 - p = 1 + \frac{(\epsilon k - z)(1 - S_e)}{2x} \quad (11b)$$

with the dose in dpa,  $\phi = kt$ . Equation (11b), therefore, gives the steady-state order as a function of dose rate.

Expression (11b) contains the equilibrium order parameter in the absence of irradiation ( $S_e$ ) which can be obtained from order-disorder transition theory (see refs. 25, 26 for reviews). Using the quasi-chemical model of Fowler-Guggenheim<sup>(27,28)</sup> and Takagi,<sup>(29)</sup> the free energy as a function of the long-range order parameter for the CsCl type superlattice is given by

$$F(S) = F(1) + \frac{k_B T}{2} \left\{ (1+S) \ln(1+S) + (1-S) \ln(1-S) - 2 \ln 2 \right. \\ \left. + Z/2 \left[ (1+s) \ln \left( \frac{\xi+S}{1+S} \right) + (1-S) \ln \left( \frac{\xi-S}{1-S} \right) - 2 \ln \left( \frac{\xi+1}{2} \right) \right] \right\} \quad (12)$$

where  $\xi = [1 + (1-S^2) (\exp(-2\Omega/k_B T) - 1)]^{1/2}$  and  $Z$  is the coordination number.

For the AuCu<sub>3</sub> type superlattice, however, this approach, using nearest neighbor pairs fails to predict an order-disorder transition. The pair theory was modified by Yang and Li<sup>(30,31)</sup> who considered a group of four atoms at a tetrahedral quadruplet of sites as the basic unit and applied the quasi-chemical model to the AuCu<sub>3</sub> type superlattice. They successfully predicted a stable superlattice below a given critical temperature. An equivalent calculation by McGlashan<sup>(32)</sup> using Yang and Li's approach for an AB<sub>3</sub> superlattice is summarized below.

$$\frac{F(S)}{k_B T} = (1/4)(3S+1) \ln \left( \frac{3S+1}{4} \right) + (3/2)(1-S) \ln \frac{3(1-S)}{4} + (3/4)(S+3) \ln \\ (3/4(S+3)) - 3 \ln 3 + \ln(a/a^*) + 3 \ln(h/h^*) + 3 S \ln \\ (cf^*/c^*f) - \frac{X_A + 3X_B}{k_B T} \quad (13)$$

The constants are

$$\begin{aligned} a^* &= (3S+1) (1-S)^3/256 \\ c^* &= (3S+1) (1-S) (S+3)^2/256 \\ f^* &= 3(1-S)^3 (S+3)/256 \\ h^* &= 3(1-S) (S+3)^3/256 \end{aligned}$$

The parameters a, c, h, f are determined by the equations

$$\begin{aligned} a &= \frac{3S+1}{4} - 3b - 3c - d \\ h &= 3/4 (1-S) - 3g - 3f - e \\ \frac{a}{\zeta^3} &= \frac{b\eta^3}{\zeta^2} = \frac{c\eta^4}{\zeta} = d\eta^3 \\ \frac{e\eta^3}{\zeta} &= \frac{f\eta^4}{\zeta^2} = \frac{g\eta^3}{\zeta} = h \end{aligned} \tag{14}$$

with  $\zeta$  given by the solution of

$$\frac{3S+1}{1-S} = \frac{(1-3\zeta^2\eta^{-4}-2\zeta^3\eta^{-3})(1+3\zeta^{-1}\eta^{-3}+3\zeta^{-2}\eta^{-4}+\zeta^{-3}\eta^{-3})}{(1+2\zeta^{-1}\eta^{-3}+\zeta^{-2}\eta^{-4})(1+3\zeta\eta^{-3}+3\zeta^2\eta^{-4}+\zeta^3\eta^{-3})} \tag{15}$$

and where  $\eta = \exp(\Omega/k_B T)$ .

The thermal equilibrium long-range order parameter  $S_e$  can, therefore, be determined by minimizing  $F(S)$  with respect to  $S$  using one or the other of these models as appropriate.

#### 2.4. Application to $\text{Cu}_3\text{Au}$

The present model of order-disorder transition under irradiation is here applied to the  $\text{Au Cu}_3$  superlattice. The resulting long-range order parameter as a function of temperature for a series of dose rates is shown in Figure 4, and the variables for this calculation are shown in Table 1.



Table 1

$\epsilon$	$\rho_d$	$Z_v$	$Z_i$	$E_v^f$	$E_{V_0}^m$	$D_0$	$(v_r v_w)^{1/2}$	$\sigma$
10	$1 \times 10^{11} \text{ cm}^{-2}$	1.0	1.02	1.28 eV	1.4 eV	$0.78 \frac{\text{cm}^2}{\text{sec}}$	$10^{13} \text{ sec}^{-1}$	0

The interstitialcy reordering mechanism is neglected by setting  $\sigma=0$  because of the large difference between the effective atomic volumes of copper and gold. The defect parameters for pure Cu are used in this calculations. The ordering energy  $\Omega$  (used in calculating  $S_e$ ) is fixed such that the critical temperature predicted coincides with the experimental value,  $T_c = 663^\circ\text{K}$ .

The values of vacancy formation energy and pre-exponent  $D_0$  are those for copper since no value is available for  $\text{Cu}_3\text{Au}$ . The value chosen for  $E_V^m$  is that found in the  $420^\circ\text{K}$  annealing stage in  $\text{Cu}_3\text{Au}$  where most of the irradiation induced resistivity anneals out thermally<sup>50</sup>. The remaining quantities in Table 1 are chosen as reasonable estimates.

Figure 4 indicates that at low enough temperatures the order parameter will always approach zero for disordering radiation because the defects are frozen-in and unable to diffuse. There is therefore no ordering reaction. At high temperatures near the critical temperatures the ordering rate due to the thermal equilibrium defect concentration dominates and radiation makes little difference except for the highest damage rates. The steady state curve then approaches the calculated equilibrium curve appropriate to the quasi-chemical model. At intermediate temperatures the radiation enhanced defects increase the ordering rate and balance the radiation disordering to give intermediate values for the order parameter.

It should be noted that at low values of  $S$  the assumption that the ordering energy is independent of  $S$  breaks down. However this only affects the thermal back reaction (i.e., the thermal disordering rate) which is

already very small at these temperatures. In any case the curves approach zero order rather rapidly and an enhancement in the disordering rate will merely decrease  $S$  a little more rapidly with decreasing temperature.

As shown in Fig. 4, a dose rate as low as  $10^{-10}$  dpa/sec is able to disorder the  $\text{AuCu}_3$  superlattice below  $\sim 430^\circ\text{K}$ . A dose rate of  $k > 1 \times 10^{-2}$  dpa is necessary to completely disorder the ordered alloy at all temperatures. A partial phase diagram under irradiation, based on these results, is shown in Fig. 5. The low temperature limit of the ordered phase is taken from Fig. 4. The remaining boundaries of the ordered region are assumed to diverge smoothly from their equilibrium positions as shown.

Several investigators<sup>(33-38)</sup> have irradiated  $\text{Cu}_3\text{Au}$ ; however, all these workers appear to have studied transient phenomena over limited dose ranges so that no measures of steady state properties have been made. Most workers monitored resistivity and the connection between this and order is not simple.

In spite of these difficulties the basic features of the theory correspond with experiment. At room temperature and below ordered alloys are progressively disordered<sup>(33)</sup> as Fig. 4 predicts. At higher temperatures highly ordered alloys disorder while disordered alloys order<sup>(33-35)</sup> indicating that the intermediate values of  $S$  predicted in Fig. 4 would eventually be attained. Since the available data does not reach steady state however the quantitative predictions of Fig. 4 cannot yet be tested.

The best data available is that of Kirk and Blewitt<sup>(33)</sup> which suggests that at  $423^\circ\text{K}$  and a dose rate  $\sim 10^{-11}$  dpa/sec of fast neutrons a value of  $1 > S > 0.5$  would be attained although the sample did not reach steady state. This result agrees very well with the curves of Fig. 4. It would be desirable to have dislocation densities available for future experiments of this type.

Given the well-known deficiencies of the quasi-chemical and chemical rate models for ordering, detailed fits to the data (especially close to the critical temperature) are not to be expected. However, viewed as a simple phenomenological approach giving physical meaning to parameters needed to fit the data, the current model is obviously attractive.

The transition from steady state disorder to order over a narrow temperature range under irradiation has also been observed in  $\text{Ni}_3\text{Fe}$ ,  $\text{Mg}_3\text{Cd}$  and  $\text{Ni}_3\text{Si}$ <sup>(51)</sup> for 1 MeV electron irradiation.  $\text{Zr}_3\text{Al}$  has shown similar effects.<sup>(9,52)</sup> The basic features of the model therefore would seem to have general application to ordered systems.

Finally, it should be noted that the irradiation induced increase in the degree of order is an example of radiation enhancement of a sluggish reaction. Figure 6 shows schematically how this can occur. Consider a phase which has not been aged for sufficient time to produce the equilibrium degree of order, the maximum order obtained is therefore less than unity ( $S_0$ ). Under irradiation, however, in the temperature range just below  $T_c$ , radiation enhanced diffusion increases the thermal reordering rate causing the steady state order parameter to lie above the original incompletely equilibrated level (Fig. 6). The arrows on the diagram indicate the direction in which the order parameter will change under irradiation.

### 3. Radiation Induced Phase Instability

The change in the order-disorder region of an alloy described in Section 2.4 is an example of an irradiation modified phase transition. When a strongly ordered intermetallic compound is in thermal equilibrium with other phases of the alloy, disordering of this ordered compound can change the whole alloy phase structure. As described in the thermal equilibrium theory of order-disorder transitions, atoms in the alloy are arranged to obtain the degree of order which minimizes the free

energy. When the alloy is irradiated, it is displaced from thermal equilibrium to a steady-state of long-range order  $S$  where the free energy is higher than this equilibrium value. Under irradiation, therefore, a new free energy balance between adjacent phases may be established giving a lower free energy than can be attained with the partially (or entirely) radiation disordered compound.

Figure 7 shows the modification of compositions of alloy phases  $\alpha$  and  $\gamma$  determined by the common tangents of free energy curves when irradiation induces an increase of free energy  $\delta F$  of the intermetallic compound  $\beta$ .

Since in the above sections the free energy of an ordered phase under irradiation has been obtained, this can be inserted into equilibrium calculations of phase diagrams containing such phases to obtain the irradiation modified phase fields. This assumes, of course, that the free energy of disordered phases is unaffected by irradiation and that they can achieve a new equilibrium when an ordered phase dissolves.

To illustrate this part of the calculation we take several systems for which calculated phase diagrams have been published and which contain strongly ordering phases. Diagrams for the systems Ti-Co, Nb-Rh and Ti-Ru have been calculated by Kaufman<sup>(39)</sup> using a set of thermodynamic data listed in ref. 39. The calculational procedure is based on sub-regular solution theory as developed by Kubachewski and co-workers,<sup>(40-43)</sup> and adopted in a set of computer programs using a wide range of thermodynamic data, by Kaufman.<sup>(39,42,43)</sup> These computer programs were modified to use the free energy of the compounds calculated from section (2), for the steady-state degree of order under irradiation using data given in table 2.

In the case of the Ti-Co and Nb-Rh systems the increase in free energy was insufficient to remove the compounds  $\text{TiCo}_3$  and  $\text{NbRh}_3$  from the phase

Table 2

	$\epsilon$	$\rho_d(\text{cm}^{-2})$	$Z_v$	$Z_i$	$E_V^f(\text{eV})$	$E_{V0}^m(\text{eV})$	$D_0(\frac{\text{cm}^2}{\text{sec}})$	$\sigma$	$E_i^m(\text{eV})$	$D_i(\frac{\text{cm}^2}{\text{sec}})$	$\Omega(\text{eV})$	$(\nu_V \nu_i)^{1/2}$ ( $\text{sec}^{-1}$ )
TiRu	10	$10^{11}$	1.0	1.02	1.6	2.0	1.0	0	-	-	0.18	$10^{13}$
TiCo <sub>3</sub>	10	$10^{11}$	1.0	1.02	1.6	2.0	1.0	0.01	0.15	0.01	0.20	$10^{13}$
NbRb <sub>3</sub>	10	$10^{11}$	1.0	1.02	1.0	2.0	1.0	0.01	0.15	0.01	0.16	$10^{13}$

(1)  $\alpha/D_i = 10^{17} \text{ cm}^{-2}$  used in all cases to compute defect concentrations (where  $\alpha$  is the recombination parameter). (24)

(2) The  $E_V^f$  and  $D_0$  of pure Ti were used as an approximation in TiRu and TiCo<sub>3</sub> and estimated values were used in NbRb<sub>3</sub> calculation.

(3) The ordering energy  $\Omega$  is obtained from thermodynamic data in Ref. 39 and is assumed to be temperature independent.

(4)  $\sigma = 0$  in the TiRu compound because the large size difference makes interstitialcy reordering unlikely. The  $\sigma$  values of 0.01 for TiCo<sub>3</sub> and NbRb<sub>3</sub> are estimates.

(5) The energies of motion of the disorder/order vacancy motion are assumed to be larger than their equivalents in the pure metals. For the purposes of calculation a factor of two has been taken (i.e.,  $E_V^m = 1 \text{ eV}$  in all cases).

diagram. Instead the phase boundary of the terminal solid solution was progressively shifted to higher solubilities, reflecting the change in common tangent contact point on the free energy curve for the terminal solutions. The limit of the effect of radiation occurs when the compound is fully disordered at lower temperatures. At intermediate temperatures the boundary lies between the thermal equilibrium value (fully ordered compound) and the higher solubility appropriate for a balance with the fully disordered compound. The separation of the phase boundary from the equilibrium position occurs at higher temperatures for higher irradiation rates as Figures 8 and 9 show. The irradiation rates chosen ( $10^{-7}$  and  $10^{-3}$  dpa/sec) are appropriate to fast reactor neutrons and heavy ion irradiations, respectively. These results show that particles of the ordered phase in the  $\alpha$  matrix will shrink under irradiation and may dissolve entirely if the alloy composition is close to the phase boundary.

The calculated equilibrium phase diagram (following Kaufman)<sup>(39)</sup> for the TiRu system is shown in Fig. 10a, and agrees closely with experiment. The diagram contains the strongly ordering compound TiRu, for which the free energy shift on disordering is particularly large since the equi-atomic composition maximizes the number of wrong bonds when disordered. The order parameter calculated from our model is shown in Figure 11, the variation of vacancy concentration at steady-state is also shown. The parameters used in the calculation are found in table 2.

The large increase in free energy as the compound disorders under irradiation, lifts the compound's free energy curve above the common tangent for the adjacent phases. A new balance state then occurs based on the mixture of these two phases ( $\beta$  and  $\epsilon'$ ) giving a new two-phase region on the diagram (Figure 10b and c). At the equi-atomic composition the

free energy of the  $\beta$  phase itself is lower than the disordered TiRu so that the  $\beta$  field extends over this range as the figure shows.

The temperature at which the TiRu phase disappears depends upon the irradiation rate. A critical degree of disorder is required to remove the phase above the  $\beta$  free energy and this depends upon the disordering rate which in turn depends upon the irradiation rate (figs. 10b and c).

The diagram shows that the disordered compound will transform to  $\beta$ . If the compound exists as particles in an  $\epsilon'$  matrix (the  $\beta+\epsilon'$  region) the new  $\beta$  phase may form by in-situ transformation of the disordered TiRu or by nucleation and growth from the supersaturated  $\epsilon'$  produced by TiRu dissolution.

The detailed mode of transformation of the destabilized compound will depend upon kinetic features which remain to be explored and are not included in the current model.

Once again the detailed numerical predictions (such as the temperature at which a phase boundary shifts or disappears) should not be regarded as accurate in detail since they depend on the parameters in table, several of which are estimated. However, the general pattern of the phase diagrams is expected to be observed.

#### 4. Discussion

##### 4.1. Examples of Radiation-Disorder Instabilities

Williams, Stiegler and Wiffen<sup>(46)</sup> irradiated w-Re alloys in EBR-II to the doses of  $6.1 \sim 37 \times 10^{21}$  neutrons/cm<sup>2</sup> ( $> 0.1$  MeV). They reported formation of  $\chi$ -phase ( $WRe_3$ ) in a single-phase (bcc W-rich solid solution) region close to the (bcc+ $\sigma$ ) phase boundary.  $\sigma$  is an ordered phase (near 50 at% Re) between the tungsten-rich bcc and the disordered  $\chi$ -phase in the thermal equilibrium phase diagram. Kaufman et al.<sup>(47)</sup> estimated the increase of the free energy of  $\sigma$ -phase necessary for the formation of  $\chi$  phase to be  $\sim 5440$  J/mole (1.3 kcal/mole). They used Maydet and Russel's theory<sup>(4)</sup>

to compute the irradiation-induced effective free energy change which turned out to be well below the value necessary for the suppression of  $\sigma$ -phase. 5 ~ 10 kJ/mole, however, could be easily attained by disordering the ordered  $\sigma$  phase resulting in its dissolution and replacement by the disordered  $\chi$  phase, as in the Ti-Ru case. Though the mechanism of the phase instability of W-Re system can now be understood, the quantitative computation of the irradiation modified phase diagram must await a complete crystallographic structure determination of the complicated  $\sigma$ -phase.

A similar disappearance of  $\sigma$ -phase has been observed in the Fe-Ni-Cr system. Brown and Cawthorne<sup>(48)</sup> were unable to detect  $\sigma$ -phase after irradiation at temperatures up to 700°C. In this range  $\sigma$ -phase is regularly observed and its presence is predicted from thermodynamic calculations. In its place a  $\gamma'$  precipitate formed. The absence of  $\sigma$ -phase has been confirmed by Bilsby.<sup>(49)</sup> Thermodynamic data are unavailable for both the  $\sigma$  and  $\gamma'$  phases at the present time. In addition, the details of the ordering arrangement in  $\sigma$ -phase are unclear. It is, therefore, not possible to calculate the ternary diagram at the present time. However, the fact that the strongly ordered, equi-atomic  $\sigma$ -phase disappears certainly suggests radiation disordering as a possible cause.

Our model so far has considered only the effect of chemical bonding in the ordered structures. The next step is the more difficult one of calculating the energy change under irradiation when the order is due to the size difference of atoms (e.g. Laves phases). Obviously, a similar phenomenology will apply but the calculation of the free energy of such phases when they are disordered by irradiation is very difficult. It seems likely that such effects will be very large, readily destabilizing such phases.



Finally, it should be noted that a large change in free energy on disordering does not guarantee a large phase diagram change. If the ordered phase is much more stable than surrounding phases even large shifts will not destabilize it entirely.

#### 4.2. Implications for Alloy Design

The calculations presented demonstrate that radiation induced disordering is capable of radically altering phase diagrams under irradiation. Since radiation disordering as a phenomenon has already been demonstrated experimentally, it is clear that we have a sound explanation for phase instabilities under irradiation.

In our model we make no attempt to improve on current theories of order-disorder; our objective has been to provide a clear conceptual framework for further experiment. Experimental results for the reordering and disordering rates under irradiation, together with the necessary thermodynamic data, are all that are required to determine phase diagrams.

From the alloy design point of view we can conclude that phases having the following characteristics are likely candidates for radiation induced destabilization.

- a) A very high ordering energy
- b) A similar stability (free energy) to adjacent phases
- c) Close to equi-atomic concentration.

Our model offers a guide to a particular type of phase stability which must be combined with solute segregation and other mechanisms to obtain an overall picture of alloy stability under irradiation. Such a comprehensive approach will require that all the various aspects described in the introduction be included. One can now begin to distinguish how this problem should be attacked within the framework of our current understanding.

Firstly, alloy design should be based on a knowledge of the true equilibrium state of the material and its approach to this equilibrium under irradiation. Secondly, solute-defect coupling should be evaluated based on measurements and theory currently available. Thirdly, second phases used to strengthen the material, or which may form under irradiation need to be evaluated. This latter step will include the model of this paper, but kinetic effects associated with nucleation of new phases stabilized by irradiation will need to be added so that radiation phase diagrams can be used to predict which phases will actually occur in practice.

Clearly, this requires a major research effort, a substantial part of which will involve measurements of basic thermodynamic properties in systems of interest.

#### 4.3. Limitations of the Model

Probably the most important assumption made in the calculations described here is that when a given compound disorders and becomes unstable with respect to a mixture of two adjacent phases, a new equilibrium will be attained. Since this involves the nucleation and growth of a new phase in the structure, whether or not equilibrium is attained depends on kinetic factors. Both nucleation and growth depend on diffusion and this will be enhanced by irradiation, because of the larger defect population. However, at very low temperatures defects will remain frozen and the new phase will be unable to form. Under these conditions the radiation phase diagram will not be obeyed and the two-phase region will be found in practice to consist of a supersaturated solution produced by the dissolution of ordered particles. The relevant free energy which the disordered compound must then exceed is that of the supersaturated matrix rather than the free energy of the two phase mixture.

Even if diffusion is permitted new phases may not nucleate. However, at this point a unified approach would consider radiation affected nucleation

which has been discussed for incoherent precipitates by Maydet and Russe<sup>(4)</sup> and for coherent precipitates by Martin.<sup>(5)</sup> In both these approaches nucleation may be either promoted or inhibited. Further discussion on the kinetics of the steady-state conditions is retained for a later paper.

Our model is also limited by the fact that we have selected a simple phenomenological approach to order-disorder so as to provide a framework for using experimental values of ordering and disordering rates under irradiation. The calculational details, therefore, rest on the assumptions of quasi-chemical or sub-regular solution theory and the long range order approximation. However, in an area of high technological interest, it is better to use simple models with phenomenological adjustment to produce detailed agreement with experiment rather than to attempt very complex ab-initio calculations with less general models.

## 5. Conclusions

1. Starting from current knowledge on the disordering of structures under irradiation we have been able to show that the free energy changes produced are sufficient to cause many ordered phases to become unstable.

2. Phase diagrams under irradiation can be calculated if ordering or disordering rates are known (together with necessary thermodynamic data for the equilibrium diagram).

3. In general at low temperature, phases which have undergone an order-disorder transition on cooling, can be forced to revert to the disordered form by irradiation. The temperature for this has been calculated for  $\text{Cu}_3\text{Au}$  as a function of dose rate.

4. Several cases of radiation phase instabilities may be explicable by this mechanism.

## 6. Acknowledgements

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Figure Captions

- Figure 1 The motion of a vacancy (o) jumping from left to right in a lattice made up of two sub-lattices ( $\alpha$  and  $\beta$  sites) can order a disordered lattice. The top line (before the jump) is disordered with B atoms on  $\alpha$  sites and A atoms on  $\beta$  sites. After two jumps (bottom line) the atoms are ordered on the sites (A on  $\alpha$  and B on  $\beta$ ).
- Figure 2 Interstitialcy motion in fcc(a) and bcc(b).
- Figure 3 Interstitial motion in the  $\text{Cu}_3\text{Au}$  type lattice. The interstitial dumbbell is ringed. Note that its motion causes an ordering with A atoms on the  $\alpha$  sites (linked by lines) and B atoms on the  $\beta$  (face centered) sites.
- Figure 4 The steady state long range order parameters of  $\text{Cu}_3\text{Au}$  under irradiation for various irradiation rates  $k$  (in dpa/sec) as indicated. The upper dashed line is the equilibrium  $S$  in the absence of irradiation as given by quasi-chemical theory. The lower parts of the irradiation curves are dashed to indicate the lower reliability of the model at low  $S$  values.
- Figure 5 The radiation modified partial phase diagram from the  $\text{Cu}_3\text{Au}$  region of the Cu-Au system. The equilibrium phase diagram is on the left and radiation modified versions of the  $\text{Cu}_3\text{Au}$  loop are plotted as a function of dose rate on the third axis. The calculated points marking the minimum temperature for the ordered region are shown as dots at the base of each loop. The sides of the loops are schematic only.
- Figure 6 Showing how in the temperature range just above point A, radiation induces an increase in order over the incompletely aged state indicated by the line marked "observed". The arrows indicate how the order varies to the right and left of point A.
- Figure 7 Showing how an ordered intermetallic compound  $\beta$  increases its free energy by an amount  $\delta F$  as it disorders to  $\beta'$  under irradiation. The new equilibrium is then indicated by the dashed tangent line A'C' between  $\alpha$  and  $\gamma$  phases. Note the change in solubilities from A to A' and B to B' when this occurs.
- Figure 8 The calculated partial phase diagram for the Ti-Co system as modified by irradiation at the damage rates shown. The original equilibrium phase boundary is the  $k=0$  line.
- Figure 9 The calculated partial phase diagram for the Nb-Rh system as modified by irradiation at the rates shown.
- Figure 10 a) The equilibrium phase diagram for the Ti-Ru system as calculated by Kaufman. (39)  
 b) The radiation modified Ti-Ru system for a dose rate of  $10^{-3}$  dpa/sec, calculated using the data in table 2 and ref. (39).  
 c) As 10b) for a dose rate of  $10^{-7}$  dpa/sec.

Figure 11 The variation of vacancy concentration  $C_v$  and order parameter  $S$ , in TiRu under a dose rate of  $k = 10^{-3}$  dpa/sec. Calculated using the data in Table 2 following the method of ref. (24). The lower branch of the vacancy concentration curve is for the equilibrium concentration.

**NOTE: figures are missing!**