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24.1. Introduction and Historical Background

Changes in properties of materials caused by irradiation have been the subject of scientific investigation for over 120 years, although they were not initially identified as such. Broegger first coined the term “metamict” to describe minerals that were optically isotropic (properties did not change with orientation) [1]. In 1914, it was discovered that these metamict minerals contained either U or Pu, and, as a result, were under constant self-ion bombardment from alpha decays. For those materials that contained more radioactive materials and that had been formed a long time ago, the damage from the alpha particles was enough to cause a complete loss of crystallinity or a crystal-to-amorphous phase transformation (amorphization) in the sample, which explains its isotropic properties. Many other similar phase transformations can be induced by irradiation as reviewed in this chapter.

In general, the significant amount of energy deposited by the energetic particles as they travel through the solid can bring about phase transformations. In the absence of irradiation, thermodynamic driving forces determine the relative stability of phases and thermally-driven kinetics (associated, for example, with point defect migration), determine the rates of phase transformations. The energetic particle flux present under irradiation can alter both the stability of phases (thus causing phases to appear that do not occur in the absence of irradiation) and the kinetics of phase transformations. These alterations in phase stability and kinetics can have profound consequences for materials behavior under irradiation. They are at the root of processes such as pressure vessel embrittlement (by the formation under irradiation of Cu-rich precipitates), irradiation induced sensitization to stress-corrosion cracking (by irradiation induced segregation and precipitation), and irradiation enhanced growth in hexagonal materials (by precipitate dissolution and nucleation of c-component dislocations). This chapter describes the alterations to the mechanisms and rates of phase transformations (stability and kinetics) caused by irradiation.

24.2 General Discussion

As discussed in Chapter 12, elastic collisions between the energetic neutrons and the atoms in the solid create recoil atoms with energies far in excess of thermal energies. This localized input of energy creates atomic structures such as defect clusters, dislocation loops, voids, etc., that are absent outside irradiation. The presence of these defects can not only alter kinetics but also phase stability. As seen in Chapter 13, under irradiation the concentration of point defects is supersaturated compared to the thermal equilibrium defect concentrations so that diffusion controlled processes are accelerated. Because the vast majority of the point defects created by atomic displacements annihilate in the microstructure of the material, large persistent fluxes of point defects to sinks are present during irradiation, which can lead to compositional variations and microstructure evolution. In addition, irradiation creates its own form of atomic transport by ballistic impact, i.e. atomic transport by impact. Finally, under a neutron flux with a thermal neutron component, such as exists in a nuclear reactor, transmutation of elements by nuclear reaction is possible, which can also alter phase stability.
Over the last forty years, experience has shown that there is no established trend that predicts the direction of irradiation-induced phase changes: stable phases can be destabilized, the approach to thermal equilibrium can be enhanced or retarded, and both irradiation-induced precipitation or precipitate dissolution can occur. Which specific changes take place depends on the irradiation conditions, material composition and initial microstructure.

Irradiation can alter phase transformations in metals and alloys under irradiation in two ways: it can accelerate the rate of the phase transformation observed outside irradiation (irradiation enhanced phase transformations) or it can cause phase transformations to occur that are not seen in the absence of irradiation (irradiation induced phase transformations). The acceleration of phase transformations under irradiation normally results from enhanced atomic transport (radiation enhanced diffusion), as discussed in section 24.3.

For ease of presentation, irradiation induced phase transformations can be divided into those that happen at constant composition and those which require compositional change.

Phase transformations at constant composition, discussed in section 24.4, can be:

a) Allotropic or polymorphic phase transformations: the crystal structure of an element (allotropic), alloy or compound (polymorphic) changes at constant composition.

b) Order/Disorder: this refers to either the loss of chemical order (disordering) or topological order (amorphization).

The phase transformations with changes in composition include precipitate dissolution or the formation of precipitates from solid solution and are normally associated with chemical composition variations induced or enhanced by irradiation, through irradiation induced segregation and/or recoil dissolution. These are discussed in section 24.5. Finally, more complex examples exist in which several of these mechanisms are combined. One example is shown in section 24.6.

No general model currently exists for irradiation altered phase transformations. Materials under irradiation are inherently in a situation far from equilibrium, and so, classical thermodynamics is of limited use in predicting the direction of phase transformations. In addition, when subjected to an external flux of energetic particles the solid cannot be considered a closed system, as it is subjected to a persistent outside input of energy and mass [2]. Because of this, materials under irradiation are considered to be forced systems, so that irradiation may take the material away from thermodynamic equilibrium or accelerate the approach to equilibrium.

Thus, it is not feasible to construct a model that accurately describes the full complexity of phase transformations under irradiation. Considering these factors, three different approximate approaches have been tried to describe phase transformations under irradiation:
1) One approximation is to replace the free energy that would be present in the absence of irradiation by a modified free energy approximately valid under irradiation (for example by considering the contribution of point defects). In this scenario, it is assumed that the phase with the lowest modified free energy would be observed [3, 4].

2) A second approximation is to describe the kinetics of the atomic transport more or less exactly and assume that the equilibrium free energy will be valid under the modified chemical potentials created by irradiation [4, 5].

3) Finally, in principle it is possible to write or derive alternative functions that replace the Gibbs free energy in predicting phase stability under specific conditions [6, 7]. The minimization of such functions would then predict the material behavior for the conditions under which the approach is valid.

Each one of these approaches can be applied with more or less success to describing the behavior of materials under irradiation. We present here a survey of specific phase transformations that can occur under irradiation and of simple models that describe them.

24.3. Irradiation Altered Kinetics: effect on atomic transport

Irradiation can alter phase transformations simply by accelerating the phase transformation kinetics, through radiation-enhanced diffusion. As mentioned in chapter 13, irradiation produces a supersaturation of point defects which increases the solid state diffusion coefficient. For example, if diffusion occurs by a vacancy mechanism, the diffusion coefficient under irradiation $D^{irr}_v$ is enhanced relative to the purely thermal value $D^\text{th}_v$ by

$$D^{irr}_v = \frac{C^{irr}_v}{C^\text{eq}_v} D^\text{th}_v$$

where $C^{irr}_v$ is the concentration of vacancies under irradiation, and $C^\text{eq}_v$ is the equilibrium concentration of vacancies under purely thermal conditions. Under this mechanism irradiation simply provides a higher concentration of defects which migrate in the same way through the lattice as do thermally induced defects. The effect of this increase in diffusion coefficient under irradiation is to enhance (or accelerate) the processes that occur outside irradiation.

Irradiation can also cause atomic motion by atomic collisions which move the atoms almost instantaneously to several lattice distances away. These jumps are usually termed ballistic jumps because of their collisional origin. This type of atomic motion is independent of temperature and will occur even at 0 K. It is possible to write a ballistic diffusion coefficient that describes diffusion for this type of process as:
\[ D_{\text{bal}}^{\text{irr}} = \frac{1}{6} k < \bar{x} >^2 \]  

(24.2)

where \( k \) is the displacement rate (dpa/s), and \( \bar{x} \) is the average distance the atoms are moved in each atomic collision.

The overall diffusion coefficient under irradiation is written as

\[ D^{\text{irr}} = D_{\text{bal}}^{\text{irr}} + D_{\text{def}}^{\text{irr}} \]  

(24.3)

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Example 24.1 Comparison of ballistic diffusion coefficient, irradiation enhanced diffusion coefficient and thermal diffusion coefficient

Compare the magnitudes of ballistic diffusion, purely thermal diffusion, and thermal diffusion enhanced by irradiation at 573 K for typical values \( (E_m^* = 1 \text{ eV}, E_f^* = 1.5 \text{ eV}, \text{ and so } Q = 2.5 \text{eV}) \).

The ballistic diffusion coefficient is given by equation 24.2. For a displacement rate of \( 10^{-6} \) dpa/s and an average displacement distance per atom of 0.5 nm we obtain

\[ D_{\text{bal}}^{\text{irr}} = \frac{1}{6} \times 10^{-6} \times \left( 5 \times 10^{-8} \right)^2 = 4 \times 10^{-22} \text{ cm}^2/\text{s} \]

For defect mediated diffusion the diffusion coefficient is given by

\[ D = D_{\text{def}} C_{\text{def}} \]

Assuming a sink dominated regime, with \( \rho_d = 10^{10} \text{ cm}^{-2} \), the \( C_{\text{def}} \) is \( 10^{-5} \) and the irradiation enhanced diffusion coefficient is

\[ D_{\text{def}}^{\text{irr}} = C_{\text{def}}^{\text{irr}} D_{\text{def}} = \frac{k}{z_{\text{def}} \rho_d D_{\text{def}}} D_{\text{def}} = \frac{k}{z_{\text{def}} \rho_d} 10^{-6} = \frac{10^{-6}}{10^{10}} = 10^{-16} \text{ cm}^2/\text{s} \]

In the case of thermal diffusion \( C_{\text{def}} = C_{\text{def}}^{\text{eq}} = \exp(-E_f / k_B T) \) and thus with an activation energy of 2.5 eV and a pre-exponential factor of 0.01 cm²/s we obtain

\[ D_{\text{def}}^{\text{th}} = D_o \exp(-Q / k_B T) = 1.04 \times 10^{-24} \text{ cm}^2/\text{s} \]
At 300ºC (573 K) the irradiation enhanced diffusion coefficient is equal to $1.6 \times 10^{-16}$ cm$^2$/s, or more than six orders of magnitude higher than the ballistic diffusion coefficient and eight orders of magnitude higher than the thermal diffusion coefficient, so that irradiation enhanced diffusion dominates under these conditions. At cryogenic temperatures, the irradiation would not be in a sink dominated regime, so that the ballistic diffusion coefficient would dominate.

***************

According to the scheme above, there are general temperature regions relating to diffusion under irradiation. At very low temperatures the thermal mobility is negligible and the only ballistic displacements cause atomic transport and so $D \approx D_{\text{ball}}^{\text{irr}}$. In this temperature regime, the diffusion coefficient is independent of temperature. At an intermediate temperature regime, the defects are mobile, and their concentration is enhanced relative to the equilibrium values, as shown in equation 24.1. In that regime, the diffusion coefficient increases with temperature and $D \approx D_{\text{def}}^{\text{irr}}$. Finally at a higher temperature regime the thermal concentrations of defects become higher than the irradiation induced concentrations and $D \approx D_{\text{def}}^{\text{thermal}}$.

When plotted in an Arrhenius plot, the three regimes appear thus:

Figure 24.1 Diffusion coefficient versus inverse temperature. The curves are plotted using $k=10^6$ dpa/s, $E^*_m=1$ eV; $E^*_f=1$ eV; $E^*_m=0.5$ eV; $D_o=0.01$ cm$^2$/s, recombination number =500, $\langle \bar{x} \rangle =5 \times 10^{-7}$ cm, and $\rho_d=10^{10}$ cm$^2$. 
The slope of the thermal diffusion (red curve) in the Arrhenius plot is equal to $-Q/k_BT$. For the low temperature regime, the slope is zero, since no thermal motion occurs. In the intermediate temperature regime (between the two dashed lines) irradiation enhanced diffusion dominates, the slope depending on the irradiation-induced defect concentration, whether in recombination dominated or sink dominated regime (the asterisk indicates the transition in this case). As shown in Chapter 13, these concentrations are different for sink-dominated (SD) or for recombination dominated (RD) regimes. For example, for vacancy migration in a recombination-dominated regime, in which only interstitials arrive at sinks the activation energy is

$$Q = E_m^v + \frac{E_m^i}{2}$$  \hspace{1cm} (24.4)

For vacancy migration in a sink-dominated regime the activation energy is zero, because the defect concentration is independent of temperature (equations 13.52 and 13.53). In the high temperature regime, the activation energy is the classical value obtained outside irradiation:

$$Q = E_m^v + E_f^v$$  \hspace{1cm} (24.5)

In the absence of irradiation, only the thermal diffusion curve in Figure 24.1 would be present. The effect of irradiation is to enable the diffusion mechanisms associated with the diffusion coefficients as shown by the blue, green and orange curves.

**24.4 Phase Transformations at Constant Chemical Composition**

Many phase transformation occurring under irradiation require neither atomic diffusion nor change in composition to take place. The transformations may involve a simple change in crystal structure or a loss of either chemical or topological order. The transformations at constant composition can thus be of three different types: (i) change in crystal structure, (ii) disordering or (iii) amorphization.

**24.4.1. Change in Crystal Structure**

Solids can exhibit different crystal structures, especially at different temperature and pressure. When these transformations refer to a single element (for example carbon to diamond) they are called *allotropic* phase transformations and when they refer to a compound they are called *polymorphic* phase transformations.

Both allotropic an polymorphic phase transformations have been reported in solids under irradiation. A polymorphic transformation of zirconium dioxide from a monoclinic structure to a tetragonal structure under ion irradiation has been reported [8-10]. Although the monoclinic phase is the most stable at the irradiation temperature, it is destabilized with respect to the high temperature tetragonal phase. One example of an
allotropic phase transformation is the transformation of graphite to diamond (in this case the high pressure phase) [11]. In each case the likely transformation mechanism is the introduction of defects in the crystalline lattice which destabilize one phase with respect to the other.

### 24.4.2 Chemical Disordering

The atomic arrangement in a crystal has a substantial degree of long-range and short-range order, both topological and chemical. As defined in Chapter 10, short-range order refers to the atomic arrangements of nearest neighbors (number, distance and bond angles) and long-range order refers to the reproducibility of the crystal over longer distances. A crystal exhibits both long-range and short-range topological order (orderly spatial arrangement of the atoms), and in a chemically ordered compound, it also exhibits chemical order (occupation of a given sublattice by the appropriate atom type).

These ordered arrangements can be destabilized by irradiation, causing disordering and amorphization. The term disordering refers to the loss of chemical order while amorphization refers to the loss of topological order. In this section we discuss both processes together, because disorder is often a necessary (although not always sufficient) condition for amorphization.

Amorphization results from irradiation induced damage accumulation such as described in Chapter 13. When a chemically ordered material is irradiated, anti-site defects are produced, in addition to vacancies and interstitials. Each defect created (point defect or antisite defect) causes slight distortions in the nearby crystal lattice. As these distortions accumulate, the lattice itself starts to lose shape, and at some point, it becomes energetically advantageous for the material to “give up” its long-range crystalline order so that short-range chemical order can be maintained. At this point, the final distortions occur that allow the material to become amorphous. Note that this is only possible in compounds that have some type of short range order to be preserved such as ordered compounds (which have chemical short range order) or materials such as Si or C, in which the interatomic bond angles constitute a type of short-range order. As a result, pure metals (which have neither chemical order nor directional bonding) do not undergo amorphization under irradiation.

As an example we show the results obtained by Hameed et al. during the irradiation of Cu₃Au using electron irradiation [12]. The Cu₃Au compound crystallizes in the L12 structure which has different crystal symmetries when ordered and disordered. This structure is shown in Figure 24.2, turning from simple cubic (ordered) to fcc (disordered).
Figure 24.2: The (L12) structure of ordered Cu3Au. Dark atoms are Cu and light atoms are Au.

Because of this change in crystal symmetry some reflections (called superlattice reflections[13]) disappear upon disordering (some reflections are not allowed in fcc that are allowed in sc) and one can follow the disordering process by following the intensity of these superlattice reflections.

Figure 24.3 (a) and (b) shows the evolution of the long range order parameter $S$ as a function of dose for various irradiation temperatures, starting from $S=1$ (a) and from $S=0$ (b). It is interesting that similar steady states of order are arrived at for each temperature, no matter what the initial state of order, whether completely ordered or completely disordered. This indicates that the steady state of order is the natural balance between displacements rate and thermal annealing and that each process can either cause ordering or disordering.

**Figure 24.3** Variation of the long-range order parameter $S$ during electron irradiation for (a) initially ordered and (b) initially disordered Cu3Au [12].

Irradiation-induced amorphization and disordering are generally not of primary importance in nuclear power applications, because the alloys used for nuclear fuel cladding and reactor structural materials do not normally undergo amorphization. The ceramics used for fuel (UO$_2$, UC, U$_3$Si) and proposed for waste disposal (ZrSi$_2$O$_4$ (zircon) for example) could potentially be disordered, however the energy cost of antisite defects in such materials is so high that this does not normally occur. The alloy Zr$_3$Al which was briefly considered as a possible material for such nuclear applications was later ruled out, precisely because of its susceptibility to amorphization [14].
Exceptions to this are second phases used in metallic alloys for either strengthening or improving corrosion resistance. Given that the original microstructure of the alloy is designed to achieve optimal performance irradiation induced changes to precipitates microstructure can compromise material performance. In particular, irradiation dis ordering and amorphization can be linked to precipitate dissolution, as exemplified in section 24.6. In the next few sections we discuss some basic models of disordering and amorphization under irradiation.

Model of Radiation Induced Disordering

The model presented here uses the change in the long range order parameter S (chapter 10) as the gauge of degree of disorder. In the simplest case, irradiation induced displacements are produced as isolated Frenkel pairs. As shown in chapter 13, in the initial stages of such a scenario the defects accumulate until their concentrations are high enough that they start interacting with each other. Once recombination starts to occur, because the Frenkel pair energies are normally higher than the chemical ordering energy, vacancies and interstitials can recombine randomly according to the following reactions:

\[ v_a + i_a \text{ or } v_b + i_b \Rightarrow \text{null} \]

\[ v_a + i_b \Rightarrow b_a \text{ anti-site defect (b atom on an a site)} \]

\[ v_b + i_a \Rightarrow a_b \text{ anti-site defect (a atom on a b site)} \]

In a recombination-dominated regime (in which most irradiation induced defects are annihilated by recombination rather than by fixed sinks), atoms are displaced from their lattice sites, and return randomly to lattice sites by recombining randomly with \(a\) and \(b\) type vacancies. These processes decrease the probability of finding an \(a\) atom in an \(a\) site \(P_{aa}\). The rate of decrease of this probability is

\[
\frac{dP_{aa}}{dt} = \left[ \text{rate of displacements from correct position by irradiation} + \right]
\]

\[
\text{rate of re-ordering by random recombination}\]

\[
= -kP_{aa} + kx_a
\]

Dividing both sides by \(1-x_a\) we obtain:

\[
\left( \frac{dS}{dt} \right)_{irr} = -kS
\]

where \(\left( \frac{dS}{dt} \right)_{irr}\) is the rate of disordering induced by random displacements, since \(S\)
(defined in Chapter 10) is \(P_{aa}x_a/(1-x_a)\). From this it follows that

\[
S = S_0 \exp(-kt)
\]
where $S_o$ is the initial degree of long range order, $k$ is the atomic displacement rate (dpa/s) and $t$ is the irradiation time. Equation 24.9 gives the variation in $S$ with dose caused by random recombination of point defects.

This disordering process is opposed by thermal reordering, which is effected by the diffusion of point defects, such that the total rate of change in the order parameter is given by

$$\frac{dS}{dt} = \left(\frac{dS}{dt}\right)_{\text{irr}} + \left(\frac{dS}{dt}\right)_{\text{th}}$$

(24.10)

There are several reordering mechanisms associated with point defect diffusion, all associated with the migration of point defects between sublattices, causing reordering as they travel through the lattice. The assumption is that the reordering jump is more probable than the disordering jump. Thus, as point defects travel through the lattice, they can leave a reordering trail behind. One such mechanism is shown below

![Reordering mechanisms](image)

(a)   (b)   (c)

**Figure 24.4:** Vacancy thermal reordering mechanisms, showing an ordering jump (a) a disordering jump (b) and a neutral jump (c).

Figure 24.4 shows the vacancy reordering mechanism. As the vacancy travels through the lattice, reordering, disordering or neutral jumps can occur. In an ordering compound, the reordering jumps occur slightly more easily than the disordering jumps, resulting in thermal reordering. The favorable configuration for a reordering jump requires a vacancy nearest neighbor to an $a$ atom on a $b$ site, as shown in Figure 24.4(a).

$$\left(\frac{dS}{dt}\right)_{\text{vac}} = \text{[ordering – disordering]} = \left[ P_{\text{ord}} \Gamma_{\text{ord}} - P_{\text{dis}} \Gamma_{\text{dis}} \right]$$

(24.11)

where $P_{\text{ord}}$ ($P_{\text{dis}}$) is the probability of finding a configuration favorable for an ordering (disordering) jump to occur while $\Gamma_{\text{ord}}$ and $\Gamma_{\text{dis}}$ are the probabilities of the respective jumps occurring. This approach was used by Zee and Wilkes [15] who derived the expression for vacancy-mediated thermal reordering during irradiation, as given by

$$\left(\frac{dS}{dt}\right)_{\text{vac}} = \left[ (Z_{ab} + Z_{ba} - 2) \frac{\nu Z_{\text{vac}} C_{\nu}}{2 x_h} \exp(-E_m / k_B T)x_a x_b (1 - S)^2 - \exp(-V / k_B T)(S + x_a x_b (1 - S)^2) \right]$$

(24.12)
where \( Z_{ab} (Z_{ba}) \) is the number of \( a \) sites nearest neighbors to a \( b \) site, \( \nu \) is the vibration frequency, \( x_a \) and \( x_b \) are the atom fractions in the compound, \( E_m \) is the vacancy migration energy and \( C_v \) is the vacancy concentration. The migration energy for an ordering jump is biased by an energy \( V^e \) (the ordering energy) towards the ordering jump so that

\[
\Gamma_{\text{ord}} = \nu e^{-\frac{(E_m^e - V)}{k_B T}}
\]  

(24.13)

where the bias \( V \) favors ordering jumps. This bias however should disappear as the lattice becomes more and more disordered, since the distinction between \( a \) and \( b \) sites disappears gradually, and thus \( V = V_v S \). The first term in curly brackets in equation (24.12) represents the disordering jumps and the second the reordering jumps.

The model above describes the disordering that can occur under irradiation if single defects are created, such as would occur under electron irradiation. Of course, cascade-producing irradiation would also cause disordering, and normally at a higher rate per dpa than electron irradiation.

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Example 24.2

It is instructive to perform a numerical evaluation and compare to experimental results. By adding up equations (24.8) and (24.12), we obtain the overall change in the order parameter as a function of dose. A steady-state is arrived at when the sum is equal to zero, that is when

\[
0 = -kS + \left[ (Z_{ab} + Z_{ba} - 2) \nu \frac{Z_{ba}}{x_b} C_v \exp\left(-\frac{E_m}{k_B T}\right) \{x_a x_b (1 - S)^2 - \exp\left(-\frac{V_v}{k_B T}\right) (S + x_a x_b (1 - S)^2)\} \right] \}
\]  

(24.14)

Equation (24.14) will be satisfied at different degrees of order for various irradiation temperatures. The final steady state degree of order was also measured by Hameed et al. as shown in Figure 24.5 below.

Insert figure

Figure 24.5 Steady state degree of order \( S \) in Cu3Au developed during electron irradiation

Although equation (24.14) cannot be solved analytically it can be evaluated numerically. The values used by Hameed et. al.[12] were

<table>
<thead>
<tr>
<th>( \nu ) (Hz)</th>
<th>( 10^{13} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_v )</td>
<td>( 5\times10^{-4} )</td>
</tr>
</tbody>
</table>
Programming these values into a calculational spreadsheet, it can be found that

Results here

24.4.3. Irradiation Induced Amorphization

By its very nature, the process of irradiation-induced amorphization is difficult to describe accurately. This is because the crystalline lattice loses its character during amorphization. Indeed, it becomes difficult to identify the nature of a defect, since the crystal in which it is defined disappears during amorphization (e.g. a vacancy is an empty spot in the crystal lattice). Because as disorder progresses the defect creation energy decreases, the process accelerates as it happens. Thus, most irradiation induced amorphization models describe the accumulation of damage to a lattice, which suddenly collapses into an amorphous structure at a critical defect density. In reality the process is gradual, but given the self-reinforcing nature of the process, the sudden collapse model is a reasonably realistic description. For a full treatment of another approach to modeling amorphization from the point of view of driven systems see [16].

Figure 24.6: The calculated free energies for the different phases in the Zr-Fe system. The dotted line is a mechanical mixture of the two elements, “s” stands for the solid solution of one element into the other and “a” stands for the amorphous phase, while the free energy curves for the Zr$_2$Fe and ZrFe$_2$ intermetallic compounds are indicated.
Model for Irradiation Induced amorphization

Outside irradiation the difference in Gibbs free energy between two phases is a measure of the relative stability of these phases. As mentioned above, one way to analyze the effect of irradiation on phase stability is to calculate the free energy increase caused by irradiation and compare this to the difference in free energy between the phases outside irradiation. Irradiation introduces point defects that change the free energy of the crystal. If under irradiation the gap between the two phases can be bridged by the damage accumulated in the form of point defects and chemical disorder, then an irradiation induced phase transformation can occur. In the case of amorphization the material can become amorphous. Clearly these are all approximate treatments, assuming for example that the free energy curves are not altered by irradiation and that the kinetics of phase transformation are fast compared to the structural changes that bring them about.

According to the argument above the condition for amorphization is then

\[ \Delta G_{irr} \geq \Delta G_{ca} \]  

(24.15)

where \( \Delta G_{ca} \) is the difference in free energy between the crystalline and amorphous phases. The condition for amorphization then is that the energy difference between the amorphous solid and the irradiated crystal become zero.

Figure 24.6 shows a calculated plot of free energy versus composition for the Zr-Fe system, which is a system of interest to nuclear applications [17]. Some of the intermetallic compounds of the type Zr(Cr,Fe)\(_2\) formed in zirconium alloy cladding have the same crystal structure as ZrFe\(_2\), with Cr substituting for Fe in solid solution in the compound, as discussed in Chapter 17. In the Zr-Fe system the free energy of a simple mechanical mixture of Zr and Fe at the composition 66 atom % Fe (point MM in the upper dotted line) is higher than the free energy of either the solid solution Fe (Zr) at that composition (\( \Delta G_s \)) or of the stable crystalline intermetallic compound ZrFe\(_2\). The calculated free energy of the amorphous solid (\( \Delta G_a \)) is higher than that of the stable crystalline intermetallic compound, but lower than any other phase at that composition. As a result when the stable phase is kinetically constrained from forming, the metastable amorphous phase becomes the second best alternative.

The difference between the two phases can be bridged by an increase in the free energy of the crystalline phase by defects accumulated during irradiation.

Modified Free energy under irradiation

The change in free energy caused by the irradiation induced defects is

\[ \Delta G_{irr} = \Delta G_{def} + \Delta G_{dis} + \Delta G_{dis\_loops} + ... \]  

(24.16)

where the right hand side terms are the individual contributions to the free energy increase from point defects, chemical disorder and from all possible irradiation-induced
defects such as dislocation loops, etc. Equation (24.16) assumes the defects are non-interacting, that is, that the defect concentration is dilute enough that one can calculate the effect of an increase in the concentration of point defects on free energy independently of the effect of an increase in the anti-site defect concentration. This is clearly an approximation, and possibly a strong one. For example, it has been demonstrated that in some compounds it is energetically favorable for a point defect of one type to become a point defect of the other type plus an anti-site defect, so that point defect annihilation can generate chemical disorder [18, 19]. However, the approximation made allows the creation of a model that explains some of the main features of irradiation induced amorphization.

The point defect contribution to free energy increase ($\Delta G_{\text{def}}$) is

$$\Delta G_{\text{def}} = \Delta H_{\text{def}} - T\Delta S_{\text{def}}$$

(24.17)

where the enthalpy difference is given by

$$\Delta H_{\text{def}} = \sum_j C_j E_{j}'$$

(24.18)

where $E_{j}'$ is the defect formation energy ($j=$interstitial, vacancy,..) and $C_j$ the defect concentration. If as in Chapter 4, we can neglect vibrational entropy, the change in entropy is given by the configurational entropy

$$\Delta S_{\text{def}} = \sum_j k_B \left[ C_j \ln C_j + (1 - C_j) \ln(1 - C_j) \right]$$

(24.19)

The chemical disorder contribution to the free energy increase is given by

$$\Delta G_{\text{dis}} = \Delta H_{\text{dis}} - T\Delta S_{\text{dis}}$$

(24.20)

Since the change in enthalpy when one $ab$ pair is lost in favor of a $bb$ or $aa$ pair is the ordering energy $V$, the enthalpy difference is given by

$$\Delta H_{\text{dis}} = \Delta N_{ab}^{\text{irr}} V$$

(24.21)

where $\Delta N_{ab}$ is the change in the number of $ab$ pairs caused by irradiation. The change in entropy is given by

$$\Delta S_{\text{dis}} = k_B \sum_k C_k \ln C_k + (1 - C_k) \ln(1 - C_k)$$

(24.22)

where the $C_k$ are concentrations of the antisite defects.

To calculate the change in free energy brought about by irradiation it is necessary to calculate the point defect concentrations as a function of fluence. This can be done using
the point defect balances developed in Chapter 13. For example, the change in the concentration of vacancies with irradiation dose in the recombination dominated regime is given by equation 13.47.

**Temperature dependence of amorphization**

Typically, a critical temperature exists above which it is no longer possible to amorphize or disorder a given compound with a given type of irradiating particle. This is because thermal reordering opposes irradiation induced disordering. The thermal reordering rate increases exponentially with temperature, while the damage rate is largely independent of temperature. At low temperatures the dose to amorphization is low (typically lower than 1 dpa). As the irradiation temperature increases, the dose to amorphization increases exponentially, because the defects that cause thermal reordering of the crystal lattice become increasingly mobile. When the reordering rate exceeds the damage rate it is no longer possible to accumulate damage and irradiation induced amorphization or disordering no longer occurs.

Figure 24.7: Dose to amorphization (dpa) versus irradiation temperature for amorphization of Zr3Fe with electrons and with Ar ions; (b) schematic curves of dose to amorphization of intermetallic compounds versus irradiation temperature for various irradiations.

This is illustrated in Figure 24.7 (a) which depicts the dose to amorphization versus temperature for Zr3Fe under electron and ion irradiation. The critical temperature for amorphization under ion irradiation is significantly higher, indicating that a higher temperature stage of defect mobility needs to be reached before annealing of cascade producing damage can occur. This is illustrated schematically in Figure 24.7 (b) which shows various increases in dose to amorphization as functions of temperature some making it harder, some making it impossible for amorphization to occur.

It is possible to derive an expression for the critical temperature for amorphization by expressing the net damage as the difference between the damage rate and annealing rate.

The amorphization condition is expressed as

\[
(k - A(T))t_{am} \geq C_{\text{def}}^{\text{crit}}
\]  

where \(A(T)\) is the temperature dependent annealing rate, \(t_{am}\) is the time to amorphization and \(C_{\text{def}}^{\text{crit}}\) is the critical defect concentration for amorphization. The dose to amorphization is then given by
\[(kt)_{am} = \frac{C_{crit}^{def}}{\sum_{j} A_{oj} e^{E_{oj}^{m}/kT} \left(1 - \frac{j}{k} \right)} \quad (24.24)\]

since \(A(T)\) is given by the sum of the annealing rates by all possible annealing mechanisms \(j\), where \(A_{oj}\) and \(E_{oj}^{m}\) are characteristic of the specific annealing mechanism considered.

To calculate the dose to amorphization it is necessary to specify the annealing mechanisms involved.

A simple annihilation mechanism is a concentration of fixed sinks. If the atomic sites in the lattice that are at the surface of absorption of a sink are expressed in atom fraction \(C_S\) then the annealing rate is

\[A(T) = C_S C_i \nu e^{-E_n^{m}/kT} \quad (24.25)\]

For a surface sink, such as would be present in a thin foil subjected to irradiation, \(C_S\) would be equal to \(\sim 3 \times 10^{-3}\) (number of surface sites divided by total number of sites for a 100 nm thick foil with atomic spacing =0.3 nm, or 660 atomic layers with 2 surfaces). If \(C_i\) is equal to the recombination dominated value given by equation 13.41, then the annealing rate is

\[A(T) = C_S \sqrt{\frac{k}{N_e \nu e^{-E_n^{m}/kT}}} e^{-E_n^{m}/2kT} = C_S \left(\frac{k \nu}{N_r}\right)^{0.5} e^{-E_n^{m}/2kT} \quad (24.26)\]

where \(N_r\) is the recombination number (equation 13.XX). Inserting (24.26) into (24.24) we get

\[(kt)_{am} = \frac{C_{crit}^{def}}{\left[1 - C_S \left(\frac{\nu}{N_r k}\right)^{0.5} e^{-E_n^{m}/2kT}\right]} \quad (24.27)\]

Equation (24.27) describes the variation of the dose to amorphization with irradiation temperature.
Figure 24.8 shows a plot of equation (24.27), for the annealing mechanism above, with $E_m^i = 0.5 \text{ eV}$, a critical defect concentration at amorphization $C_{def}^{crit}$ of 0.01, vibration frequency $= 10^{13} \text{ Hz}$, and a recombination number of 200, for two displacement rates: $10^{-4} \text{ dpa/s}$ (dotted line) and $10^{-3} \text{ dpa/s}$ (solid line). It can be seen that at low temperature the dose to amorphization is 1 dpa, since the annealing rate is negligible. Near the critical temperature the dose to amorphization increases abruptly as the annealing rate becomes higher than the displacement rate. For the displacement rate of $10^{-4} \text{ dpa/s}$ this occurs at about 260 K while for a displacement rate of $10^{-3} \text{ dpa/s}$ this occurs about 290 K.

![Figure 24.8: The dose to amorphization as a function of irradiation temperature for two displacement rates: $k=10^{-3} \text{ dpa/s}$ and $10^{-4} \text{ dpa/s}$](image)

The critical temperature for amorphization can be obtained by setting the damage rate equal to the annealing rate

$$k = A(T) = A_o \exp(-E_m^i / k_B T)$$  \hspace{1cm} (24.28)

$$T_{crit} = -\frac{E_m^i}{2k_B} \frac{1}{\ln \left( \frac{k}{A_o} \right)}$$  \hspace{1cm} (24.29)

For the example above,

$$A_o = C_s \sqrt[3]{\frac{k}{N_v v e^{-E_m^i / k_B T}}}$$  \hspace{1cm} (24.30)

and thus
\[
T_{\text{crit}} = -\frac{E_m'}{2k_B} \ln \left[ \frac{1}{C_S \left( \frac{N_i k}{\nu} \right)^{0.5}} \right]
\]  
(24.31)

which for the values in Figure 4.29 yields critical temperatures of 288 K and 258 K for \( k=10^{-3} \) and \( 10^{-4} \) dpa/s as shown in the plot.

**The Law of Corresponding States**

An alternative and interesting way to describe irradiation induced amorphization is to use the law of corresponding states, derived by G. Martin [7]. A mean field description of the evolution of a system subjected to both ballistic jumps and thermal jumps for regular solid solutions yields the simple result that the effect of the introduction of ballistic jumps is to increase the entropy of the system, which is equivalent to a temperature rise.

This results in the law of corresponding states which predicts that the solubility limit observed under irradiation at temperature \( T \) is that observed outside irradiation at a temperature \( T' \) given by:

\[
T' = (1 + \Delta)T
\]

(24.32)

where \( \Delta = \frac{\tilde{D}_b}{\tilde{D}_{th}} \) with \( \tilde{D}_b \) and \( \tilde{D}_{th} \) the ballistic and thermal chemical diffusion coefficients.

The same formalism can be extended to amorphization, by imagining that a steady state amorphous solution will be observed when the dose rate necessary to cause amorphization is that for which \( T' > T_{\text{melt}} \).

Example 24.3 Critical temperature for Amorphization using law of corresponding states

Calculate the critical temperature for amorphization of the intermetallic compound Zr\(_2\)Ni if it melts congruently at 1120° C (1393 K) when irradiated at a dose rate of \( 10^{-3} \) s\(^{-1} \) and \( 10^{-4} \) s\(^{-1} \). Assume that the activation energy for thermal motion is 0.8 eV.

The calculation can be done using \( D_0 = 0.01 \) cm\(^2\)/s and a ballistic distance of 10 A. The results are shown in Figure 24.9 which shows the effective temperature calculated using equation 24.33 for displacement rates of \( 10^{-2} \) and \( 10^{-3} \) s\(^{-1} \). When these effective temperatures under irradiation become equal or higher than the melting temperature, the crystal can undergo amorphization under the specific irradiation conditions, and when they fall below the melting temperature amorphization can no longer occur.

The actual observed critical temperature for electron irradiation induced amorphization Zr\(_2\)Ni is about 250-260 K, in agreement with the calculations above. Note that there is a slight effect of dose rate, (the critical amorphization temperature increases slightly with dose rate) which was also observed experimentally [20].
Disordering under Cascade Producing Irradiation

The critical temperature for amorphization under ion irradiation is considerably higher than that for electron irradiation, as was shown in Fig. 24.7 [21, 22]. This is commonly attributed to the presence of displacement cascades, such that processes such as direct amorphization in the cascade core become possible [21]. In displacement cascades defect clusters can be formed directly and the density of the damage is much higher so that annealing mechanisms are correspondingly less efficient.

One possible model for cascade disordering is to assume that in the molten zone of a cascade, complete disordering occurs, and that this disorder is preserved by the rapid quenching of the cascade by the surrounding material that follows. In that case, chemical disordering is caused by an accumulation of impacts eventually causing complete coverage of the material. Each cascade amorphizes a volume equal to $V_c$ by direct impact. This is reflected by the fact that it takes $kt$ displacements to cause amorphization in $Bkt$ of the atoms where $B$ is a constant smaller than 1. As the material is successively hit, the
probability of hitting pristine material decreases exponentially such that the crystalline fraction $f_c$ is given by

$$\frac{df_c}{dt} = -Bk f_c$$  \hfill (24.15)

$$f_c = e^{-Bkt}$$  \hfill (24.16)

The amorphous fraction is simply the complement of the crystalline fraction

$$f_a = 1 - f_c = 1 - \exp(-Bkt)$$  \hfill (24.33)

The amorphous fraction is seen to depend both on the parameter $B$ and on the dose in dpa. If amorphization requires two cascades to overlap for an amorphous zone to be created the amorphous fraction is given by

$$f_a = 1 - f_c = 1 - \left[ (1 + Bkt + (Bkt)^2/2) \exp(-Bkt) \right]$$  \hfill (24.34)

The amorphous fractions predicted by the two models are shown in Figure 24.10. The black and blue curves show the amorphous accumulation from a single impact model and the red curve shows the amorphization kinetics predicted by a double impact model.
24.5. Phase Transformations with Changes in Composition

Phase transformations under irradiation can also involve changes in chemical composition. Under thermal conditions, such changes in composition require atomic transport by diffusion. Under irradiation, many effects are superimposed that can cause chemical composition to vary, depending on the starting microstructure. On the one hand, the irradiation flux generally tends to take the material in the direction of greater entropy, and thus cause elemental mixing, causing existing precipitates to dissolve. On the other hand irradiation establishes strong and persistent defect fluxes which can interact with solutes causing solute segregation and possibly precipitation.

Clearly, irradiation-induced segregation is of great technological importance, since most alloys used in power reactors are complex alloys containing more than one component. Since the material properties are optimized at fabrication, and the distribution of solute additions affects material behavior, modifications to the microchemistry of the alloy can impact the properties of the material, usually in a deleterious manner. Two examples, among many, of the possible technological impact of irradiation induced segregation are:

a) During neutron irradiation austenitic steels can exhibit Cr and C segregation to the grain boundaries causing carbide precipitation and a depletion of Cr from the matrix nearby the grain boundary. This process sensitizes the steel to stress-corrosion cracking.

b) The light elements Si and Be which are added for increased swelling resistance in austenitic steels and nickel based alloys for fusion first-wall applications, can segregate to the wall surface, thus negating the beneficial effect of these elements (curiously, the loss of swelling resistance is somewhat compensated by the creation of a beneficial low Z coating of the inner wall, which helps reduce sputtering).

c) Some alloys such as Zircaloy-4, alloy X-750, and oxide dispersion strengthened steels rely on second phase precipitates for their good properties, be it corrosion resistance (Zircaloy-4), or mechanical properties. The possible disappearance of these precipitates as a result of exposure to neutron irradiation could change these material properties for the worse.

In this section we review the processes of precipitate dissolution and of radiation induced segregation and precipitation.

24.5.1. Irradiation Induced Precipitate Dissolution

Precipitates that would normally be stable under purely thermal conditions can be destabilized and dissolved under irradiation. Several mechanisms are possible for precipitate dissolution: in the core of a cascade, atoms can be ejected from a precipitate particle into the matrix, a process called recoil dissolution; also, the enhanced defect
concentration present under irradiation (either in the precipitate or in the matrix) can change the equilibrium between precipitate and matrix and cause precipitate dissolution. Section 24.6 shows another example in which irradiation induced amorphization destabilizes the precipitate.

Recoil Dissolution

The process of recoil dissolution is akin to the resolution of fission gas bubbles into the matrix. The basic idea is that the large energies given to recoil atoms mix the atoms of the precipitate with those of the matrix, in the region close to the precipitate-matrix interface. This “homogenization” process, in which the atoms from both phases are mixed randomly across the interface, is opposed by the thermodynamic tendency of the solute atoms to attach themselves to the precipitates. If the displacement rate is high enough, or if the temperature is low enough, however, the rate of re-clustering is less than the rate of irradiation mixing and the elements in the precipitate are dispersed into the matrix.

A simple model of recoil precipitate dissolution can be conceived by picturing a distribution of spherical precipitates subjected to an irradiation flux.

\[ \ell = N_p^{-0.33} \]

\[ r_{eq} \]

\[ R_e \]

Figure 24.11: Model for irradiation induced precipitate dissolution

We assume a binary alloy, with an overall solute content of \( x_S \). Initially the solute is distributed in \( N_p \) (cm\(^3\)) precipitates, each with a solute concentration of \( C_p \) and in the matrix where the solute solubility is \( C_m \) (Fig. 24.11). If the precipitates are evenly distributed, then each precipitate is at the center of a unit cell, of side \( \ell = 1/(N_p)^{0.33} \). It is clear that in this situation the solute flux at the boundary of the unit cell is zero. This reduces the problem to a redistribution of solute within the cell. To further simplify the problem, we define an effective sphere radius \( R_e \) with the same volume as the box above.
The rate of growth or dissolution of the precipitates is then given by the net atom flux (atom/cm².s) that crosses the surface of the precipitates:

\[
\frac{dn}{dt} = J_+ - J_-
\]  

(24.36)

where \( n \) is the number of solute atoms in the precipitate and \( J_+ \) and \( J_- \) are the solute atom fluxes into and out of the precipitate. The dissolution flux \( J_- \) results from the mixing imposed by cascades that hit close enough to the precipitate-matrix interface that the recoils thereby produced can be ejected from the precipitates into the matrix. For a precipitate of radius \( r \), this flux is:

\[
J_- = 4\pi r^2 \frac{k \mu}{4}(C_p - C_m)
\]

(24.37)

where \( k \) is the displacement rate (dpa/s), \( \mu \) is the average range of recoils, \( C_p \) and \( C_m \) are the atomic percent of solute in the precipitates and in the matrix respectively. Here we make the assumption that the precipitate-matrix interface is flat on the scale of the displacements cascade.

The re-precipitation flux results from back diffusion of the material from the matrix towards the precipitates,

\[
J_+ = 4\pi r D_S C_m
\]

(24.38)

where \( D_S \) is the diffusion coefficient of solute in the matrix. If the overall atomic percent of solute in the alloys is \( x_S \), we can write:

\[
x_S = \frac{4\pi r^3}{3} C_p + \frac{4\pi(R_e^3 - r^3)}{3} C_m
\]

(24.39)

Solving for \( C_m \)

\[
C_m = \frac{x_S - \left(\frac{r}{R_e}\right)^3 C_p}{1 - \left(\frac{r}{R_e}\right)^3}
\]

(24.40)
At equilibrium, the forward and backward fluxes are equal, so that setting (24.38) equal to (24.37) we find an equation for the equilibrium radius \( r_{eq} \)

\[
4\pi r_{eq}^2 \frac{k\mu}{4} (C_p - C_m) = 4\pi r_{eq} D_s C_m
\]  
(24.41)

substituting for \( C_m \)

\[
\frac{D_s}{r_{eq}} \left[ x_s - \left( \frac{r_{eq}}{R_e} \right)^3 C_p \right] \left[ k\mu r_{eq} \right] \left[ 1 - \left( \frac{r_{eq}}{R_e} \right)^3 \right] = \frac{k\mu}{4} \left[ 1 - x_s \right] C_p
\]  
(24.42)

and

\[
r_{eq}^2 = \frac{3}{4\pi N_p} \left[ x_s - \frac{k\mu r_{eq} C_p}{4} \left[ 1 - x_s \right] \frac{r_{eq}}{D_s} \right]
\]  
(24.43)

Note that for \( k=0 \) we have

\[
N_p \frac{4\pi r_{eq}^3 C_p}{3} = 1, x_s
\]  
(24.45)

as expected (all the solute is precipitated). Equation 24.43 can be solved exactly to yield

\[
r_{eq} = \frac{-B}{3u} + u
\]  
(24.45)

where

\[
u = \left[ \frac{-C}{2} \pm \sqrt{\frac{C^2}{4} + \frac{B^3}{27}} \right]^{1/3}
\]  
(24.46)

and
The equilibrium radius \( r_{eq} \) given by equation 24.47 is plotted versus displacement rate in Figure 24.12, for three values of the solute diffusion coefficient, and using typical values of the parameters \( N_p=1\times10^{11}\text{cm}^{-3},\ C_p=0.66,\ x_S=0.01 \). For a sufficiently high value of the diffusion coefficient the precipitate radius is unchanged by recoil dissolution. For lower values the equilibrium precipitate radius decreases with increasing displacements rate.

![Figure 24.12: Equilibrium radius for a precipitate subjected to recoil dissolution as a function of displacement rate for three values of the solute diffusion coefficient. \( x_S=1\% \) and \( C_p=66\% \).](image-url)
Figure 24.13 shows the ratio of the equilibrium precipitate radius under irradiation \( r_{eq} \) to the precipitate radius outside irradiation \( r_o \) as a function of the parameter \( \frac{k\mu}{D_s} \). When \( \frac{k\mu}{D_s} \) increases, the displacement rate becomes much higher than the diffusion coefficient and the equilibrium precipitate radius becomes much smaller than the radius outside irradiation.

**Increased solubility in the matrix**

Another possibility for precipitate dissolution induced by irradiation is for the solute solubility in the matrix to increase under irradiation. Rearranging equation 24.38 we obtain a precipitate radius of

\[
r_{eq} = \left( \frac{x_s - C_{m, irr}}{C_p - C_{m, irr}} \right)^{\frac{1}{3}} R_e
\]

(24.45)

As the solid solubility increases, the precipitate size decreases. When the solid solubility under irradiation \( C_{m, irr} \) is > \( x_s \), the precipitates disappear.

In this section we considered the effect of mixing induced by irradiation leading to smaller precipitate size or to complete dissolution. Under irradiation it is also possible to observe the opposite effect (elemental segregation followed by precipitation and coarsening) as explained in the following sections.
24.5.2 Irradiation Induced Segregation and Precipitation

The study of solute segregation under irradiation was motivated by several experimental results showing segregation of alloying elements towards or away from grain boundaries, dislocations, external surfaces, voids and other fixed defect sinks, during high temperature irradiation. In many cases the local concentration is increased locally to values that exceed the terminal solid solubility, so that precipitation can occur even from globally undersaturated solid solutions.

Mechanism and temperature dependence

Segregation under irradiation occurs by the coupling of defect fluxes to solute atoms, creating a solute flux. The vast majority of defects created during irradiation annihilates either by recombination with the opposite defect, or by absorption at fixed sinks. As a result, persistent defect fluxes, (of an overall magnitude approximately equal to the defect creation rate) are established during irradiation. Given the high doses of 1-10 dpa that some reactor core components suffer during service, the total number of defects arriving at sinks during reactor exposure is enormous. Because of this, when the defect fluxes pass through a solid solution on the way to annihilation at defect sinks, even a small coupling of the defects to the solute atoms will cause preferential enrichment or depletion of these solutes at the fixed sinks.

The process is illustrated on Figure 24.14. At the start (a) the solute is evenly distributed inside a grain of the material with a concentration \( C_{sol} \) and the defect concentrations are the thermal equilibrium concentrations \( C_{def}^{eq} \). When irradiation starts (b) the defect creation rate by the particle flux becomes > 0 (\( \phi > 0 \)) (b) and a higher steady state defect concentration \( C_{def} \), characteristic of processes under irradiation is established. At a later time (c) these defects start to be absorbed at fixed sinks (in this example grain boundaries) which creates a defect concentration gradient leading towards the sinks. In this example, the interaction of the defects with the solutes (c,d) causes these to be enriched at the grain boundary, with a corresponding solute depletion zone nearby. As the solute is depleted from the grain and enriched at the grain boundary, a driving force is created for a back diffusion flux away from the grain boundary, and which ultimately limits the amount of segregation. As the irradiation induced segregation proceeds, the depleted zone is extended (d) and the level of depletion increased. At the same time the concentration of solute at the grain boundary locally surpasses the solubility limit and precipitation occurs. Once the precipitates are formed, this creates a further barrier for back diffusion as the solute is tied up in the precipitates and dissolution has to occur, before the solute is free to migrate. The grain boundary precipitates can then grow to a larger size (e).

Since the process depends on long range diffusion on defects to sinks, when point defect recombination is the dominant defect annihilation process, no irradiation induced segregation occurs in the recombination dominated region. Also, because irradiation induced segregation is a non-equilibrium phenomenon, at high temperatures thermal back diffusion negates the non-equilibrium segregation imposed by irradiation. This causes
Irradiation induced segregation to occur in a relatively narrow temperature window, between 0.3 and 0.5 $T_m$. The temperature window varies with dose rate. This is illustrated schematically in Figure 24.15, which shows the temperature window for irradiation induced segregation as a function of dose rate; higher dose rates tend to increase the lower and upper bounds of the temperature window.

Figure 24.14: The process of irradiation induced segregation illustrated schematically (see text).
Figure 24.15 Schematic diagram showing the region of incidence of radiation induced segregation in terms of homologous temperature and as a function of displacement rate [23].

This type of temperature dependence is common to many different irradiation effects which disappear at high temperature (because of increased annealing) and at low temperature (because of increased recombination). Unfortunately, reactor operating temperatures tend to fall in the regions where these effects are maximized, as illustrated in Fig.24.15.

Lam and Johnson Theoretical Formulation

The model currently used in the literature is due to Johnson and Lam [24]. It calculates solute segregation occurring during irradiation due to the interaction of solutes with point defect fluxes, obtained from solving the point defect balance equations.

\[
\frac{\partial C_i}{\partial t} = \nabla J_i + k - K_{iv} C_i C_v
\]  \hspace{1cm} (24.4)

\[
\frac{\partial C_v}{\partial t} = \nabla J_v + k - K_{iv} C_i C_v
\]  \hspace{1cm} (24.5)

The equations above are similar to those in Chapter 13, with the exception that the sink terms are taken into account explicitly in the boundary conditions. In other words, the geometry of the sinks needs to be considered as a spatial redistribution of solute is what is being studied.
In order to travel through a lattice composed of A and B atoms, vacancies have to exchange place with either A or B atoms, and interstitials have to be either A or B type.

\[ J_i = J_i^A + J_i^B \]  \hspace{1cm} (24.6)
\[ J_i = -(J_v^A + J_v^B) \]  \hspace{1cm} (24.7)

where \( J_i^A \) and \( J_i^B \) are the flux of A and B interstitials and \( J_v^A \) and \( J_v^B \) are the fluxes of vacancies via A and B atoms. It is also true that \( J_v^A = -J_v^B \) and \( J_i^A = J_i^B \) and the same for B atoms. The flux of A atoms is written as

\[ J_A = J_A^i - J_A^v \]  \hspace{1cm} (24.8)
\[ \frac{\partial C_A}{\partial t} = \nabla J_A \]  \hspace{1cm} (24.9)

In the Lam-Johnson formulation the defect fluxes are written as

\[ J_i^A = -D_i^A \alpha \nabla C_A - D_i^A \nabla C_i \]  \hspace{1cm} (24.10)

where \( \alpha = \left[ 1 + \frac{\ln \gamma}{\ln x_a} \right] \) is the thermodynamic coefficient and \( C_B = 1 - C_A \).

The equations above can be solved, for example, within a grain with the initial conditions \( C_A \) and \( C_B \) constant for all \( x \) and with the boundary conditions \( C_i = C_v = 0 \) at the grain boundary. This formulation can be extended to systems with multiple components and also to systems with concentrated solutions. The individual diffusivities, effective solute-defect binding energies and thermodynamic coefficients have to be known independently or evaluated from data. Once these are known then predictions of the amount of segregation can be made and compared to data. The equations however quickly become complex, and the solutions depend strongly on the binding energies and the parameters assumed.

**Examples of Radiation Induced Segregation**

Radiation induced segregation has been observed in many systems. The technique normally used for detecting is transmission electron microscopy, in a microscope that has an energy dispersive x-ray spectroscopy attachment. This allows the determination of chemical composition from measuring the energy spectra of the x-rays induced by the electron beam. The amplitude of the characteristic x-ray peak of an element or the area under the peak can be correlated, at least semi-quantitatively with the element concentration. If a small enough probe can be obtained, and the grain boundary can be
tilted to be parallel to the beam a precise profile of grain boundary segregation can be obtained.

Figure 24.16: Concentration profile of several elements near a grain boundary in a stainless steel [25]

Such a concentration evolves with dose, and different elements are segregated to or away from the grain boundary as shown in Figure 24.24.[26]

Figure 24.17: Average grain boundary concentrations for Fe-20Cr-24Ni proton irradiated at 400C to doses up to 3 dpa
Another example of precipitation under irradiation which has great technological implications is the pressure vessel embrittlement caused by Cu-rich precipitates formed under neutron irradiation and which is discussed in Chapter 25.

### 24.6. A Complex Example: Irradiation Induced Changes to Second Phase Precipitates in Zircaloy

We have so far treated these processes of amorphization, disordering and precipitate dissolution more or less independently. However, they are clearly intertwined in real cases, as shown in the example described here.

It has been observed that some intermetallic precipitates in Zircaloy undergo amorphization under neutron irradiation. The transformation has been observed in Zircalloys irradiated at 550 to 620 K (from both LWR fuel cladding and structural material)[21]. After reactor exposure in this temperature range, although the Zr$_2$ (Ni,Fe) precipitates are completely crystalline, the Zr(Cr,Fe)$_2$ precipitates are partially amorphous. In fact they develop a "duplex" structure, consisting of an amorphous layer that starts at the precipitate-matrix interface, and which gradually moves into the precipitate with increasing neutron fluence until the precipitate is completely amorphous. This is shown in fig.24.11.

![Transmission electron micrograph of a partially amorphous Zr(Cr,Fe)$_2$ precipitate in Zircaloy 4 irradiated to $4 \times 10^{21}$ n/cm$^2$](image1.png)  
![Chemical composition variation across a partially amorphous precipitate](image2.png)

**Figure 24.18.** Precipitate amorphization and dissolution under neutron irradiation: (a) transmission electron micrograph of a partially amorphous Zr(Cr,Fe)$_2$ precipitate in Zircaloy 4 irradiated to $4 \times 10^{21}$ n/cm$^2$ (Courtesy C. Regnard, CEA) (b) chemical composition variation across a partially amorphous precipitate [27]

A crystalline core (marked “C”) is present in (fig.24.18(a)), as evidenced by the stacking fault contrast, while an amorphous layer (marked “A”) has been formed that will
eventually comprise the whole precipitate. Interestingly, chemical analysis of the precipitates after the amorphous layer is formed shows that Fe is lost from the amorphous region to the Zr matrix, as shown in Figure 24.18(b). A region of lower Fe concentration is established which coincides with the amorphous ring of the precipitate. Amorphization is associated with a depletion of iron from the amorphous layer into the Zr matrix, while the Cr concentration in the precipitate remains constant.

This process provides an interesting example of complex coupled processes occurring during neutron irradiation of alloys. The width of the crystalline core shown in Figure 24.18 was measured by various researchers and found to increase linearly with fluence [28]. These observations (amorphization starting at the precipitate edge, the layer advancing at a rate proportional to fluence and the loss of Fe to the Zr matrix) can be explained by a model which describes amorphization caused by an increase in free energy caused by irradiation.

The change in free energy caused by irradiation, given in equation (24.16) is valid for an infinite solid. In the case of precipitates in a matrix, the mixing of atoms at the interface caused by the ballistic displacements will cause a departure from stoichiometry at the interface. Such a departure from stoichiometry is energetically costly for intermetallic compounds, since the free energy increases steeply with the departure from stoichiometry. This is the reason for preferential amorphization at the precipitate-matrix interface: a small departure from the exact stoichiometry causes a large increase in free energy, which causes that interface region to reach the amorphization condition first. The amount of mixing is the integral of the net flux of solute (Fe and Cr) across the precipitate-matrix boundary.

\[
J = J^+ - J^-
\]  

(24.46)

If the maximum recoil distance is \(< x_m >\), then recoils originating up to that distance from the interface can leave the precipitate into the matrix, via a knock-on mechanism. If the displacement rate is \(k\) dpa/s then the flux out of the precipitate is

\[
J^+ = \frac{1}{2} \int_0^{x_m} C(x)k(1 - \frac{x}{x_m})dx
\]  

(24.47)

If it is assumed that departures from stoichiometry equivalent to \(\delta c\) are enough to cause amorphization then the concentration at the crystal-amorphous interface (\(x=0\)) is \(C_o-\delta c\). Given that the sputtering probability decreases linearly with distance from the interface and that \(C(x) = C_o\) at \(x=x_m\) (no variation from initial concentration) and \(C=C_o-\delta c\) at \(x=0\), then

\[
C(x) = C_o - (1 - x / x_m)\delta c
\]  

(24.48)
Substituting equation (24.48) into equation (24.47) and performing the integration yields

\[
J^+ = \frac{1}{4} k x_m \left[ C_o - \frac{2}{3} \Delta C \right]
\]

(24.49)

This process is illustrated in Figure 24.19. The result is that the amorphization process is controlled by the flux-driven departure from stoichiometry at the interface. As a consequence, the boundary between the amorphous and crystalline parts advances at a rate proportional to the flux, and thus the thickness is proportional to fluence, as observed.

Figure 24.20 shows a schematic plot of free energy variation with concentration for phases in the ZrFe-Cr system, including the Zr hcp phase, the crystalline Zr(Cr,Fe)\(_2\) precipitate and the amorphous Zr(Cr,Fe)\(_2\) precipitate. It is clear that a small variation in concentrations in the crystalline precipitate causes a large variation in free energy.

Thus, the outward flux described in equation (24.49) causes a change in precipitate stoichiometry, which in turn causes precipitate amorphization to start at the precipitate-matrix interface. Once an amorphous layer is formed, the Fe concentration in the amorphous precipitate is no longer in equilibrium with the Zr matrix. This is illustrated in Figure 24.20 which shows the free energy of the precipitate before and after irradiation. As the precipitate accumulates damage in the form of point defects and disorder induced by irradiation, its free energy increases at nearly constant concentration (varying by only about \(\delta c\)) from point A to point B, at which point the precipitate turns amorphous.

The Fe content in the amorphous precipitate at point B is no longer in equilibrium with the matrix, and thus it loses Fe, following the bold red arrow to re-establish a common
tangent equilibrium at a lower Fe content. As a result, significant Fe depletion from the precipitate into the matrix occurs.

Figure 24.11: Quasi-equilibria established under irradiation for the amorphous phase and the matrix.

Thus, in this case, the interplay of chemical equilibria, irradiation dissolution, departure from stoichiometry and differential mobility of atoms in the crystal cause a remarkable amorphization process to take place, followed by alloying element dissolution. The consequences of this alloying element increase in the matrix can be substantial, as shown in Chapter 27.

Problems

24.1. The intermetallic compound ZrCr2 undergoes irradiation and may undergo amorphization. It is desired to calculate the critical transformation temperature above which amorphization cannot occur.

a. Calculate the ratio of ballistic to thermal jumps for a case where $k=10^{-3}$ dpa/s, the average recoil distance is 1 nm and the activation energy for thermal motion is 0.9 eV with $D_0=0.02$ cm$^2$/s.

b. Calculate the critical temperature for amorphization if the compound melts congruently at 1673°C (1946 K).

24.2. A precipitate under irradiation undergoes amorphization and dissolution under a displacement rate of $10^{-4}$ dpa/s. The mechanism is based on irradiation induced increase in point defect concentration and irradiation induced disordering. In this instance, upon becoming amorphous the precipitate becomes unstable and quickly dissolves. It is desired to calculate at which dose the precipitate would undergo amorphization and dissolution.
Assume that the rate of disordering is given by

\[ S = S_0 e^{-kt} \]

where \( S \) is the long range order parameter, \( k \) is the displacements rate and \( t \) is the irradiation time and the initial order parameter is 1. Assume further that the concentrations of vacancies is given by

\[ \rho_i = \frac{z_D^2}{K_{iv}} K_{iv} (D_i) \]

where the dislocation density is \( 10^{10} \text{ cm}^{-2} \), \( K_{iv} \) is \( 3 \times 10^{16} \text{ cm}^{-2} \). The change in free energy is given by

\[ \Delta G = \Delta G_{\text{def}} + \Delta G_{\text{dis}} = H_{\text{def}} C_{\text{def}} + \frac{NV}{3} (1 - S^2) + \frac{2}{9} (1 - S) \]

where \( NV = 4000 \text{ J/mol} \) and \( H_{\text{def}} = 157618 \text{ J/mol} \). The free energy change necessary to cause amorphization is \( 6000 \text{ J/mol} \).

a) Calculate the change in order parameter with dose. After how many seconds will \( S \) be equal to 1%?
b) In an Excel spreadsheet calculate \( \Delta G_{\text{def}} \) and \( \Delta G_{\text{dis}} \) as a function of time. Plot them both along with their sum against time.
c) At what time would amorphization occur? How would the answer change if \( k = 10^{-7} \text{ dpa/s} \)?

24.3. One possible process of irradiation induced amorphization in the case of cascade-producing irradiation is amorphization by direct impact. It is desired to evaluate the amorphization kinetics due to such a process. To do so, assume that amorphization occurs at very low temperature (no annealing), and that each cascade impact creates a volume \( v_a \) of amorphous material upon quenching of the cascade. As the cascades become more numerous, they will start impinging on each other, because the remaining crystalline is smaller. Assume you are irradiating 1 cm\(^3\) of material and that cascades are produced evenly throughout the material

a) Write an expression for \( df_a/dt \), that relates the amorphous fraction \( f_a \) (=total volume amorphous/total volume) to the irradiation flux \( \Phi \), the scattering cross section \( \sigma_s \) and the irradiation time.
b) Analytically integrate that expression to find \( f_a = f(t) \)
c) If the scattering cross section is 20 barns, the amorphous volume per cascade is 1000 \( \text{nm}^3 \), and the ion irradiation flux is \( 10^{13} \text{ ion.cm}^{-2}.s^{-1} \), calculate the time to achieve 99\% amorphization.
24.4. A Zr-4at\%Fe alloy is irradiated at 300 C. At this temperature outside irradiation essentially all iron is precipitated, but irradiation provides a driving force for dissolution. It is desired to use the law of corresponding states to evaluate when dissolution would occur. This means calculating an effective temperature at which dissolution would occur.

a) From the phase diagram below, what would be this effective temperature for Zr-4at \%Fe and why?

b) According to the law of corresponding states, under what displacement rate (dpa/s) would total dissolution of Fe in Zr be expected? If we assume Z=6, jump distance =0.323 nm, migration energy 1.6 eV and the average recoil distance \( <x> = 5 \) nm.

24.5. Show that for a solid in which defects are being created at a rate of \( k \) dpa/s and in which random recombination of vacancies and interstitials is taking place, the long range order parameter is given by \( S=S_o \exp(-kt) \)
References


