Chapter 13: Microstructure Evolution under Irradiation

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13.1 Introduction

In the previous chapter we have seen how irradiation with energetic particles creates a population of point defects and defect clusters issuing from the debris of the displacement cascades. After they are created, stable point defects can migrate thermally (see chapter 4), and eventually react (be absorbed, annihilated or to cluster) with other microstructural features such as other point defects, defect clusters, dislocation loops, voids and other lattice defects.

The accumulation of these defects in the material is limited by the processes of defect recombination, clustering and annihilation at defect sinks. Because the rates of defect generation are quite high, relative to the number of point defects that can be sustained in the lattice, under irradiation a large number of defects is constantly being annihilated at sinks. Since the defects have to thermally migrate through the material to arrive at sinks, one of the main effects of irradiation is to cause persistent and significant defect fluxes that permeate the material while it is subjected to the energetic particle flux. One can well speak of a “vacancy wind” or an “interstitial wind”, because it is the effect of the motion of the defects, the persistence of high defect fluxes, rather than higher concentrations of the point defects themselves that causes the largest impact on the material.

The interaction of the defects and the defect fluxes with the irradiation-induced microstructure are at the origin of the processes of microstructural evolution which cause the macroscopically measurable irradiation effects. These in turn can affect material performance, by changing mechanical properties, material dimensions, and causing phase transformations. We present in this chapter the relevant physical processes and the rate theory methodology that allows us to describe this microstructure evolution under irradiation.

13.2 Phenomena Relevant to Microstructure Evolution under Irradiation

Figure 13.1 illustrates the processes occurring during exposure of a metal alloy to cascade producing irradiation, and that can lead to an evolution of the microstructure. In the upper right hand corner a displacement cascade is shown creating a number of defects and defect clusters (1). The very high number of displacements in the cascade can cause new phases to appear (disordering, amorphization) where the cascade hits, sometimes requiring two or more cascades to hit (2). The vacancy rich core in the cascade can collapse into a dislocation loop (3) or remain as a depleted zone (1). After the intra-cascade clustering and defect interaction has produced the final defect configuration, these isolated defects can then migrate to extended sinks. The interaction of these defects with the sink structure creates a steady state concentration of defects that is higher than the equilibrium concentration outside irradiation (4).
Vacancies and interstitials can react with each other (recombination (5)), in which case, both defects disappear without any further effect on the material. The recombination

![Diagram of physical processes involved in microstructure evolution under irradiation](image)

Figure 13.1. Physical processes involved in microstructure evolution under irradiation

reaction can be enhanced by trapping of defects at solutes (6). Point defects can also interact with other defects of the same type, which causes defect clusters to form and grow (7). The defect clustering and absorption in the material changes the original microstructure, creating voids and loops, such that the sink density and strength at the beginning is modified all along the irradiation.

As shown in the figure, interstitials and vacancies also migrate through the material and are absorbed at extended sinks such as network dislocations (8) (present from the material fabrication process), voids (9) (formed under irradiation), incoherent precipitates (10) and grain boundaries (11). Some of the defects absorbed in dislocations can cause dislocation climb, which is one of the mechanisms for irradiation creep. Preferential interaction of the defect fluxes with solute atoms (12) can cause solute enrichment near or away from defect sinks (e.g. grain boundaries, (13)), creating non-equilibrium local supersaturations that can lead to grain boundary precipitation of new phases (14). At the same time, cascade atomic mixing puts atoms of existing precipitates back into solid solution in the matrix (15), which can destabilize and dissolve precipitates.
The processes shown in Fig. 13.1 are a mix of “athermal” processes such as (2) and (15) and thermally activated processes such as (5), (7) and (8). In general, microstructural evolution is also a mixture of (i) processes that depend on long-range thermal migration such as defect assisted dislocation climb, (ii) processes that depend on short-range atomic rearrangements, and (iii) processes that are completely athermal. Because of this, the effects of radiation, resulting from the interaction of radiation damage with microstructure evolution, depend on the balance between radiation damage and thermal annealing.

For the thermal processes, a reduction in the overall energy of the material takes place when these defect-defect and defect-sink reactions. The recombination of interstitials and vacancies is the most obvious example, causing a Frenkel pair of overall energy about 5 eV to completely disappear and reform the perfect lattice. However, reactions such as divacancy formation and defect absorption at dislocations also cause the energy of the material to diminish. For the athermal processes, as discussed above, the collision energies are so high that processes such as irradiation induced dissolution or amorphization can occur in spite of causing an overall increase in free energy.

All these processes happen in parallel, and compete and interact with each other. For example, if the rates of recombination and absorption at voids are matched at some point, the absorption leads to void growth, which eventually could destabilize the balance in favor of further void growth.

As a way of treating the complex phenomena described above, we homogenize the microstructure (create an equivalent medium with the same defect creation and reaction rates) to arrive at spatially independent kinetic equations. This is done in the next sections. We should note, however, that spatial correlation of damage can be, in fact, very important. Even if defects are completely free to undergo long range migration after a cascade cools down, the probability that a vacancy will interact with the interstitials formed in the same cascade is considerably higher than average. Also, although in this simpler formulation of rate theory we consider an isotropic solid, for many phenomena (such as irradiation growth, see chapter 19) the crystallographic distribution of damage and annealing is crucial.

**13.3 Rate Theory Formulation of Defect Evolution Under Irradiation**

The complex interactions of the defects with the microstructure shown in Figure 13.1 are difficult to model explicitly, especially in the vicinity of the extended defects, where defect gradients exist. The rate theory formulation [1] calculates the bulk defect concentrations in the material by performing more or less explicit calculations of the reaction rates and sink strengths and averaging them over the material, in effect “smearing them out” so that the whole solid is homogeneous.

The approach used is to calculate the reaction rates of point defects with other defects and with extended sinks, taking into account the local geometry of these...
interactions. By then combining the locally calculated defect-sink reaction rates with the overall sink density and defect generation rate, it is possible to write equations that describe the variation of the microstructure in terms of chemical rate processes. These equations can then be used to calculate the concentrations of defects and the consequent microstructural evolution for different irradiation conditions.

13.3.1. Basic Rate Theory Assumption

Many reactions are possible between point defects and fixed or extended sinks in the material. Those are all competing reactions, and their relative rates will determine microstructural evolution. In the classical rate theory model, these are modeled as first order chemical reactions, i.e., for any species $A$ and $B$ of concentration $C_A$ and $C_B$ (atom fraction) in the solid:

\[
\text{Rate of reaction between species } A \text{ and species } B \text{ (reaction/atom)} = K_{AB} C_A C_B \tag{13.1}
\]

that is, the reaction rate is characterized by a rate constant $K_{AB} \text{ (s}^{-1})$, which is assumed independent of the defect concentration and generation rate (but that could be dependent of temperature, defect geometry, migration path, etc.) and is linearly dependent on the concentration of the defects. The reaction rate is given in units of reactions per atom per second. As shown later, $K_{AB}$ is written as $K_{AB} = \xi_{AB} (D_A + D_B)$, where $\xi_{AB}$ is a geometric factor and $D_A$ and $D_B$ are the diffusion coefficients of species A and B.

We distinguish two types of reactions: defect-defect reactions and defect-extended sink reactions. In the first case, be it clustering or recombination, the nature of the defect is changed, for example a divacancy is formed from two vacancies, or the elimination of the defects upon recombination. In the second case, the defect disappears by being absorbed into a sink. For example, upon the interaction of an interstitial with a free surface, the interstitial disappears as a separate entity and creates a surface with a small imperfection.

In the following are some of the reactions considered here, written in chemical reaction form:

**Point Defect Recombination** ($K_{iv}$ : recombination rate constant ):

\[
v + i \xrightarrow{K_{iv}} \text{null} \tag{13.2}
\]

**Vacancy Clustering** ($K_{vv}$ : divacancy formation rate constant ):

\[
v + v \xrightarrow{K_{vv}} 2v \tag{13.3}
\]

\[
v + 2v \xrightarrow{K_{2v}} 3v, \ldots \text{etc}
\]

**Interstitial Clustering** ($K_{ii}$ : di-interstitial formation rate constant )

\[
i + i \xrightarrow{K_{ii}} 2i \tag{13.4}
\]
\[ i + 2i \xrightarrow{K_{2v}} 3i, \ldots \text{etc} \]

Defect Absorption at Sinks (\( K_{sj} \) rate constant for absorption of defect \( j \) at sink \( s \))

\[ \begin{align*}
  \text{sink} & \xrightarrow{K_{si}} \text{modified" sink} \\
  i & \xrightarrow{K_{si}} \text{"modified" sink}
\end{align*} \] (13.5)

13.3.2 Reaction Rate Constants

We now calculate the individual rates of defect reactions both between point defects and fixed sinks in the material.

Reactions Between Point Defects

In reactions between defects the reaction rates are calculated by noting that there is a distance of close approach under which the defects react athermally, without the need for a thermal jump. The sites around the defect from which this happens are the athermal reaction volume (the athermal reaction volume increases with the energy difference between the reagents and the reactants, i.e. for divacancy formation, the reaction volume is equal to the defect configuration itself, while for interstitial-vacancy recombination it is much larger.) It follows then that the rate of reaction is equal to the probability of finding a defect at one jump distance from the athermal reaction volume, times the probability that a favorable jump occurs.

Divacancy formation

The reaction under consideration here is the initial step of vacancy cluster formation, i.e. the formation of a di-vacancy from two individual vacancies (equation 13.3)

\[ \text{sink} + \text{sink} \xrightarrow{K_{sv}} \text{2sink} \]

The reaction described goes preferentially from left to right because the final configuration has a smaller total energy than the two separate vacancies, i.e; \( E > E' \) in fig.13.1. For example in Fe the divacancy formation energy is *** while the vacancy formation energy is **.
Given a material that has \( C_v \) vacancies (atom fraction) the rate of divacancy formation per atom is

\[
\text{rate of divacancy formation per atom} = P_{vv} C_v
\]  

(13.6)

where \( P_{vv} \) is the probability per unit time that a vacancy in one of the second-nearest-neighbor positions to another vacancy jumps into a nearest neighbor position, thus forming a divacancy. This probability is given by the product of the favorable configurations for a jump and the jump rate:

\[
P_{vv} = Z_1 Z_2 C_v w
\]  

(13.7)

where \( Z_1 \) is the number of nearest neighbors to the vacancy, \( Z_2 \) is the number of lattice positions for each of the first nearest neighbor from where a vacancy can jump into the first nearest neighbor sites. Then \( Z_2 C_v \) is the probability that a favorable configuration exists for the jump (i.e.) a vacancy in one of the sites next to a nearest neighbor site, ready to perform the atomic jump that will create a divacancy. \( Z_1 w \) is the jump probability for the favorable configuration described above.

So the rate of divacancy formation from two individual vacancies is:

\[
\text{rate of divacancy formation per atom} = Z_1 Z_2 C_v^2 w
\]  

(13.8)

From chapter 4, the jump rate is \( w = \nu e^{-\frac{E_v}{kT}} \). Since from the rate theory assumption expressed in equation 13.1, the reaction rate is \( K_{vv} C_v^2 \), then we identify the reaction rate constant as

\[
K_{vv} = \text{number of favorable sites x jump probability} = Z_1 Z_2 w
\]  

(13.9)

**Example 13.1:**

Calculate the rate constant for divacancy formation for the fcc lattice. Figure 13.2 shows the relevant geometrical configuration. There are twelve nearest neighbor sites in the fcc...
lattice and thus $Z_1 = 12$. For each of the nearest neighbor sites there are in turn twelve nearest neighbor sites. Of these, one is the original vacancy and five are shared with that vacancy and thus jumps from these sites are eliminated. The remaining seven are sites from which a jump into the nearest neighbor site considered would create a divacancy from two separate vacancies. Thus, $Z_2$ is equal to 7 and the rate constant for divacancy formation in the fcc lattice is

$$K_{vv} = 84w$$

but since both vacancies are equally mobile, the rate is twice as high,

$$K_{vv} = 168w$$

![Diagram showing di-vacancy formation reaction in fcc lattice](image)

**Figure 13.2. Di-vacancy formation reaction in fcc [2].**

**end of example 13.1**

**Point Defect Recombination**

Vacancies and interstitials also have a rate constant for recombination similar to that for the formation of divacancies from single vacancies. In view of the fact that vacancy-interstitial recombination results in a perfect lattice (defects are annihilated), the amount of energy relaxed is considerably higher, so the number of sites from where recombination can occur athermally is higher than the geometrical size of the defects. As seen in the previous chapter, if an interstitial finds itself within a region around the vacancy called the recombination volume, recombination occurs spontaneously without need for thermal motion. Because the energy relaxed upon recombination is quite high
(~5eV), the region around the vacancy from where athermal recombination can occur can comprise many hundreds of atoms.

By analogy with the divacancy derivation

\[ K_{iv} = \text{number of favorable sites} \times \text{jump probability} = P_{iv}w \]  

(13.10)

The number of favorable configurations is computed in a similar way to the divacancy derivation above, but in a less straightforward way because of the different geometry. In this case, the critical rate-determining jump is the jump from the outside to the inside of the recombination volume. Thus \( Z_1 \) is number of sites within the recombination volume but next to its outer surface and \( Z_2 \) is the number of sites outside the recombination volume from which a jump could occur to each of the \( Z_1 \) sites.

The number of favorable configurations for a recombination jump is then

\[ P_{iv} = C_v \cdot Z_1 \cdot Z_2 \cdot C_i \]  

(13.11)

The jump probability is given by the sum of the two defect mobilities \( w = w_i + w_v \sim w_i \). In metals normally the interstitial migration energy is much lower than the vacancy migration energy and thus \( w_i \gg w_v \). Since the three dimensional configuration of sites \( Z_1 \) and \( Z_2 \) is complicated, we give below a two dimensional example of the calculation of \( Z_1 \) and \( Z_2 \).

**Example 13.2**

Calculate the recombination rate constant for the schematic 2D recombination volume configuration below, if the nearest neighbor jump frequency is \( w \).

*Figure 13.3: Schematic two dimensional configuration of an athermal recombination volume around a vacancy (dotted line), showing the three different types of sites.*

The schematic 2D configuration shown in Figure 13.3 shows three different types of \( Z_1 \) sites, four of each type for a total of 12. As seen in the figure, the number of \( Z_2 \) sites is different for each type. For sites type 1, there are four \( Z_2 \) sites; for sites type 2 there are two and for sites type 3 there is one.
The total number is thus \(4 \times (4+2+1) = 28\) possible jumps per vacancy leading to recombination and thus \(K_{iv} = 28w\). Clearly, for a 3D case, the total possible number of jumps would be much higher leading to a higher value of \(K_{iv}\).

**close example 13.2**

In the general case, the total number of favorable configurations is given by

\[
P_{iv} = C_i C_j \sum_{all \ j} Z_{2j}
\]

(13.12)

where \(j = \) all sites \(Z_i\). Thus the recombination reaction rate is

\[
\text{Recombination rate} = C_i C_j w_i \sum_{all \ j} Z_{2j} = C_i C_j w_i N_r
\]

(13.13)

and the recombination rate constant is \(K_{iv} = w_i \sum_{all \ j} Z_{2j} = w_i N_r\) where \(N_r\) is the recombination number. The values of the summation over all possible configurations can range from 50-500. Typical recombination numbers could be on the 100s.

### 13.3.3. Reactions with Extended Sinks

In the case of reactions of point defects with extended sinks, the reaction rates are calculated by using the geometric shape of the sink and considering that diffusion limits the defect ingress into the sink. We consider that near the extended sinks the defect concentration is kept near the thermal equilibrium value and well far away from the sink it is equal to the bulk average value.

In the derivations in this section sinks are considered to be inexhaustible, i.e. we consider that the absorption of defects does not appreciable change the sink. However, we note also that the sink strength of extended sinks can evolve with irradiation. For example, an incoherent precipitate with a larger volume than the matrix has a volume mismatch with the matrix, and is a sink for vacancies, as the vacancies help eliminate strain energy. However, as vacancies are absorbed, the mismatch decreases until the precipitate is no longer a vacancy sink. In contrast, the sinks considered in this chapter do not change with irradiation.

**Point Defect Absorption by Dislocations**

Point defects are absorbed at dislocations because there is a net elimination of lattice strain energy during the reaction. The actual defect absorption eliminates the defects and causes a small jog to appear in the dislocation line (the additional energy from the jog is much smaller than the vacancy formation energy \(E_{f}\)). After many absorptions of one type of point defect the cause the dislocation line will climb. In its
simplest form the absorption of point defects by dislocations is modeled in rate theory in the following way.

1. The dislocation distribution is represented by the dislocation density $\rho_d$. This assumes an even distribution of dislocation lines in the material and only one type of dislocation defect, whereas in reality the distribution of dislocations is very anisotropic and inhomogeneous, and many different types of dislocation can exist.
2. There is a region next to the dislocation line, the dislocation core, into which defects enter but do not exit.
3. The effects of the presence of the dislocation line on the concentration of defects diminish such that at a distance $R_d$ the concentration of defects is equal to $C_{v,\text{bulk}}$.
4. Within the radius of influence of the dislocation, the defects undergo random walk, with no influence of the dislocation strain field.

The absorption of defects at the sinks is limited by the diffusion of defects into the dislocation core, because the absorption reaction is much faster than the defect transport. By considering that dislocations are evenly spaced we obtain that each dislocation has an associated cylinder of radius $R_d$ given by equation 6.**

$$\pi R_d^2 = \frac{1}{\rho_d} \quad \therefore \quad R_d = \frac{1}{\sqrt{\pi \rho_d}}$$

So each dislocation has a "claim" on all defects inside "its" cylinder. The dislocation core, radius $r_o$ acts like a black hole (all defects that wander into it "stick" and are absorbed).

![Figure 13.4: Geometry for the derivation of the reaction rate for defect-dislocation line interaction](image)
We assume that the defect generation rate in the cylinder is negligible during the diffusion of the defect from $R_d$ to $r_o$. Since there is symmetry in the theta and z directions, the defect concentration depends only on $r$ and the balance equation in the region affected by the dislocation is:

$$\frac{1}{r} \frac{d}{dr} \left( r \frac{dC_v}{dr} \right) = 0$$

(13.14)

which is to be solved with the following boundary conditions

(i) $C_v(r_o) = C_v^{eq}$

(ii) $C_v(R_d) = C_v^{bulk}$

(13.15)

The solution comes from integrating equation 13.14 and applying the boundary conditions.

$$\frac{C_v - C_v^{eq}}{C_v^{bulk} - C_v^{eq}} = \frac{\ln(r/r_o)}{\ln(R_d/r_o)}$$

(13.16)

The vacancy flux to the dislocation per unit dislocation line is then given by

$$J_{v}^{\text{dis}} = 2\pi a \left[ D_v \left( \frac{dC_v}{dr} \right) \right]_{r_o}$$

(13.17)

Substituting equation 13.16 into 13.17 we obtain

$$J_{v}^{\text{dis}} = 2\pi \frac{D_v C_v^{bulk}}{\ln(R_d/r_o)}$$

(13.18)

Since there are $\rho_d$ cm of dislocation line per cm$^3$, we obtain

$$J_{v}^{\text{dis}} \rho_d = 2\pi \rho_d \frac{D_v C_v^{bulk}}{\ln(R_d/r_o)} = z_v \rho_d D_v C_v^{bulk}$$

(13.19)

where $z_v = \frac{2\pi}{\ln(R_d/r_o)}$ = dislocation bias for vacancies $\sim 1$, for reasonable values of the dislocation core radius and dislocation density.

Assumption 4 is less valid for interstitials, which interact more strongly with the dislocation than vacancies. A practical way of dealing with the problem is to assume a larger effective radius of influence for the interstitial-dislocation interaction than for the vacancies. That is $R_d^i > R_d^v$, and this increase is not directly related to $\rho_d$, i.e. it is not found by using equation 6.*, and is simply a means of artificially increasing the range of interaction between interstitials and dislocations.
and thus $K_{\text{disl-i}} = z_i \rho_d$ and $K_{\text{disl-v}} = z_v \rho_d$. Because of this difference, dislocations are biased sinks for interstitials.

This simplified analysis gives an idea of the defect absorption process in dislocations. This analysis can also be used for dislocation loops, although the geometry is somewhat different (essentially $\rho_d$ is used, and no consideration to geometry is given—dislocations are straightened out).

**Point Defect Absorption at Voids**

Similar arguments for point defect absorption can be made in the case of voids. The configuration is:

![Figure 13.5 Geometry for calculation of defect absorption at voids](image)

In a solid containing $N$ voids per unit volume, the volume associated with each void is equal to $1/N$, and thus the defects within that volume will be absorbed at that void. The radius of the sphere of the volume equivalent to $1/N$ is

$$R_d = \left[ \frac{3}{4\pi N} \right]^{\frac{1}{3}}$$

(13.21)

The diffusion of defects within the volume $1/N$ into the void at the center controls the defect absorption at voids. Clearly this defect concentration will be only dependent on $r$, and the appropriate equation is
\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_v}{\partial r} \right) = 0
\]  
(13.22)

With the boundary conditions

(i) as \( r \to R_d \), \( C \to C_{v bulk}^v \)  
(13.23)

(ii) as \( r \to R \), \( C \to C_{eq}^v \)

The solution is

\[
C_v(r) = C_{v bulk}^v + \left( C_{v bulk}^v - C_{eq}^v \right) \frac{R}{R_d - R} - \frac{R}{1 - R/R_d} \left( C_{v bulk}^v - C_{eq}^v \right) \frac{1}{r}
\]  
(13.24)

If \( R_d \to \infty \) then we obtain a simpler form

\[
\frac{C_v(r) - C_{v bulk}^v}{C_{v bulk}^v - C_{eq}^v} = \frac{R}{r}
\]  
(13.25)

and

\[
\frac{\partial C}{\partial r} = \frac{R}{r^2} (C_{v bulk}^v - C_{eq}^v)
\]  
so that

So the rate of defect absorption per void is:

\[
J_{v void} = 4\pi R^2 D_v \left. \frac{\partial C}{\partial r} \right|_{r=R} = 4\pi R D_v \left[ C_{v bulk}^v - C_{eq}^v \right]
\]  
(13.26)

Since there are \( N \) voids per unit volume, the rate of vacancy and interstitial absorption into voids per second per atom is

\[
J_v^{void} = 4\pi R D_v (C_{v bulk}^v - C_{eq}^v) N
\]  
(13.27)

\[
J_i^{void} = 4\pi R D_i (C_{i bulk}^i - C_{eq}^i) N
\]

The same technique can be applied to grain boundaries and free surfaces (see problem 13.4).

13.3.4. Reaction rates and Sink Strengths

In the derivations above we expressed the flux of defects to sinks as a product of reaction rate constants and densities. The reaction rate constant is given as

\[
K_{ks} = \xi_k D_k
\]  
(13.28)
where $\xi_k$ is a geometrical factor for the absorption of defect $k$ into a sink and $D_k$ is the diffusion coefficient for defect $k$. This formulation is useful in that it parallels the expressions obtained for point defect reactions, which is why it was adopted here. However it is often useful to express the reaction rate in terms of sink strengths, i.e.:

$$\text{Reaction Rate} = K_{ks} C_s C_k = \xi_k D_k C_s C_k = S_{ks} D_k C_k$$

(13.29)

where $S_{ks} = \xi_k C_s$ is the sink strength in the material. For example for dislocations and voids the interstitial sink strengths are $z, \rho_d$ and $4\pi R N$, respectively. The sink strength provides a useful measure of the ability of a material to absorb defects into extended sinks.

### 13.4. Defect Generation Rate (dpa/s)

In the point defect balance equations, it is necessary to postulate a defect creation rate. In the case of neutron irradiation, this procedure leads to the approximate equation 12.41

$$k_{NRT} \approx \phi \frac{\sigma_s (E_n)}{5E_d} N(E_n)$$

where the scattering cross sections can be obtained from an appropriate database such as ENDF-VI [3].

In the case of charged particle irradiation, the energetic particle flux is normally monochromatic, and the calculation is somewhat simpler. For ion irradiation the use of a code such as SRIM [4] can provide an accurate representation of the displacement cross section. Thus

$$k_{ion} = \frac{\sigma_d^{TRIM}}{N_{target}} \phi_{ion} [dpa/s]$$

(13.30)

TRIM gives the displacement cross section $\sigma_d^{TRIM}$ in units of displacements/ionÅ. To obtain displacements per atom per second it is necessary to divide by $N_{target}$, the number of atoms in a 1 cm$^2$ x 1 Å layer in the material.

For electron irradiation a further simplification is warranted in that electrons interact only once within a thin foil in an electron microscope, so no energy loss calculation is needed and the displacement rate is simply

$$k_{el} = \phi_e \sigma_e^{e} [dpa/s]$$

(13.31)
Tabulations of the electron displacement cross section as a function of displacement energy, electron energy and atomic number were prepared by Oen [5] using the McKinley-Fesbach relativistic cross section.

### 13.5 Point Defect Balances and Solutions

Except for the athermal effects resulting from the direct impact of displacement cascades, the surviving point defects are the agents of microstructural evolution under irradiation. As noted previously, point defect concentrations are greatly enhanced under irradiation, compared to the thermal equilibrium concentrations calculated in chapter 3. The elimination process of this point defect supersaturation, their migration through the lattice and subsequent annihilation, clustering or recombination, is what causes the observable irradiation effects. To evaluate radiation effects it is, therefore, essential to estimate the point defect concentrations during irradiation and their annihilations rates at sinks.

#### 13.5.1. Point Defect Balance Equations

The local change in defect concentration of the various defect species can be written as the result of local production rate, reaction rates and a diffusion term. The relevant reactions were listed in page 13.** and consist of defect creation, clustering, absorption at sinks and defect trapping. The point defect balances are then:

\[
\text{Rate of Change} = \text{Generation} - \text{Divergence of Flux} - \text{Recombination} - \text{Annihilation} - \text{Clustering}
\]

If clustering is considered, then system of equations is open, i.e., \(v \rightarrow 2v \rightarrow 3v\) ... In that case one equation has to be written for each of the cluster sizes. If for the moment, these reactions are neglected then the rate equations can be written:

\[
\frac{\partial C_v}{\partial t} = D_v \nabla^2 C_v + k - \sum_s K_{vs} C_s C_v
\]

\[
\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + k - \sum_s K_{is} C_s C_i
\]

where \(D_v\) and \(D_i\) are the defect diffusion coefficients, \(k\) is the defect generation rate, \(C_i\) and \(C_v\) are the defect concentrations in atom fraction, \(C_s\) are the sink densities (cm\(^{-2}\)) and the \(K_{is}\) are the sink reaction rates (cm\(^2\)/s).

Such equations require boundary conditions and initial conditions to be solved. In specific cases where the spatial distribution of defects is important, the equations (13.32) and (13.33) can be solved in their spatially dependent form (see 13.6). In most cases, however, this equation is used in its spatially independent form. If that is the case:

\[
\frac{\partial^2 C_v}{\partial t^2} = k - \sum_s K_{sv} C_s C_v
\]

\[
\frac{\partial^2 C_i}{\partial t^2} = k - \sum_s K_{vi} C_i C_s
\]
The rate coefficients $K_{iv}, K_{vi},$ etc. for the several reactions were developed in the previous sections. For example, for the case of defect absorption at voids and dislocations, we have

$$\frac{\partial C_i}{\partial t} = k - K_{ii} C_i C_v - z_i \rho_d D_i C_i - 4 \pi R N D_v C_v$$ \hspace{1cm} (13.36)

$$\frac{\partial C_v}{\partial t} = k - K_{iv} C_i C_v - z_v \rho_d D_v C_v - 4 \pi R N D_i C_i$$ \hspace{1cm} (13.37)

This closed form of the point defect balance equations is particularly useful to illustrate the development of point defect concentrations under irradiation under various conditions and to identify the relevant regimes of operation.

### 13.5.2 Solutions of Point Defect Balances

Given the previous formulation, the next step is to solve the defect balance equations for simple cases. The quantities of interest are the defect concentration as a function of time, the concentration at steady state, and the time to steady state. In the following, we assume that one defect is fast and one is slow, which given the differences in migration energy between interstitial and vacancy is always somewhat true. In metals the migration energy of the interstitials is usually much lower than that of the vacancies, and thus we assume $D_i >> D_v$. The equations are coupled and non-linear and as a result they have no analytical solution, and are normally solved numerically. Because the differences between the coefficients in the equations are often orders of magnitude, a robust equation solver is needed, and often the equations have to be made appropriately non-dimensional in order to avoid roundoff errors.

We now follow the temporal evolution of the defect concentrations in the solid under irradiation. The treatment follows that of Sizmann [6]. At the beginning, point defects are created in what is essentially a defect-free solid. The point defects are few and they do not interact with each other. During that stage the interstitial and vacancy concentrations accumulate at the rate $kt$, and:

$$C_i = C_v = kt$$ \hspace{1cm} (13.38)

Depending on the microstructure of the material, the damage rate and the irradiation temperature, one of two types of processes - defect elimination at sinks or recombination of interstitials and vacancies - limits the accumulation expressed in 13.38. If defect absorption at sinks limits accumulation, then we have a sink-dominated regime, whereas if recombination limits accumulation we have a recombination-dominated regime.

Because interstitials and vacancies are homogeneously distributed throughout the material, the diffusion length for recombination is much smaller than for absorption at sinks. As a result, as the temperature decreases, the importance of recombination also increases. The time in-between displacement damage events also plays a role, i.e. if the...
displacement rate is high, the defects have less time to arrive at sinks and therefore recombination is also favored with respect to sink absorption. Finally as the sink density increases, the spacing between sinks decreases and consequently the mean free path for absorption also decreases, causing sink absorption to increase.

In summary, recombination tends to dominate for low temperature, high displacement rate, low sink density microstructures and vice-versa for sink absorption. We now consider these two limits separately.

Recombination Dominated Regime

Figure 13.5 shows the graphic illustration of the processes that we describe below.

\[
\log C \\
\begin{array}{|c|c|c|c|}
\hline
\text{Defect Buildup} & \text{Recombination} & \text{Fast Defect (Interstitial)} & \text{Slow Defect (Vacancies)} \\
\text{without Reaction} & \text{Dominates} & \text{arrives at Sinks} & \text{Arrives at Sinks} \\
\hline
C_i = C_v = k t & C_i = \frac{k}{K_{iv}} & C_i = \frac{k t \sum_k K_i C_s}{K_{iv}} & C_i = \frac{k \sum_k K_{iv}}{K_{iv} \sum_k K_{iv}} \\
\hline
\tau_1 = \frac{1}{kk_{iv}} & \tau_2 = \frac{1}{\sum_k K_{iv} C_s} & \tau_3 = \frac{1}{\sum_k K_{iv} C_s} & \\
\hline
\hline
\end{array}
\]

Figure 13.5: Defect concentrations as a function of time in a recombination dominated regime.

If recombination limits the defect accumulation, the characteristic time for recombination to influence the process \( \tau_1 \) is obtained by:

\[
\frac{dC}{C} = 0 = k - K_{iv} C^2 , \text{ since } C_i = C_v = k t
\]  
(13.39)

\[
\tau_1 = \frac{1}{kk_{iv}}
\]  
(13.40)
After $\tau_1$, recombination exactly balances production and thus no further increases in defect concentration occur. The defect concentrations are then frozen at

$$C_i = C_v = k \tau_1 = \frac{k}{K_{iv}}$$

(13.41)

If recombination were the only process for defect elimination, this would be the final steady state. However if other sinks are present, they eventually influence defect accumulation. At time $\tau_2$ the fast defect (interstitial) starts to arrive in significant quantities at the defect sinks. As the interstitials start to get eliminated at sinks, their concentration in the lattice decreases. This leads to a decrease in recombination and to a corresponding increase in vacancy concentration. The characteristic time for interstitial arrival at the sinks is found by setting

$$\frac{\partial C_i}{\partial t} = -\left(\sum_s K_{si} C_s\right) C_i$$

(13.42)

The characteristic time for this exponential process is

$$\tau_2 = \frac{1}{\sum_s K_{si} C_s}$$

(13.43)

This ushers in a period when interstitials arrive at sinks but vacancies do not, and in which the defect concentrations are given by:

$$C_i(t) = \sqrt{\frac{k \left(\sum_s K_{si} C_s\right) t}{K_{iv}}}$$

(13.44)

$$C_v(t) = \sqrt{\frac{k}{K_{iv} \left(\sum_s K_{si} C_s\right)} t}$$

(13.45)

The vacancy concentration builds up until their concentration is so high that even with their reduced mobility they start arriving at sinks at time $\tau_3$,

$$\tau_3 = \frac{1}{\sum_s K_{sv} C_s}$$

(13.46)

After $\tau_3$ the vacancy concentration is high enough that the flux of vacancies unto sinks matches the interstitial flux and this brings about the final steady state in the recombination dominated regime. At the final steady state the defect concentrations are

$$C_i = \frac{k \sum_s K_{sv}}{K_{iv} \sum_s K_{is}} \text{ and } C_v = \frac{k \sum_s K_{is}}{K_{iv} \sum_s K_{sv}}$$

(13.47)
Thus the respective defect concentration are related through their reaction rates with the 
sinks

\[
\frac{C_v}{C_i} = \frac{\sum_s K_{iv}}{\sum_s K_{vi}}
\]  

(13.48)

In the case of neutral or nearly neutral sinks equation 13.44 reduces to

\[
D_i C_i = D_v C_v
\]

(13.49)

That is, the defect concentrations are in the inverse relation of their mobilities. We note 
that the defect concentrations are proportional to the square root of the displacement 
damage rate. This means that for a process that depends linearly on the defect 
concentration, changing the rate by a factor of 2 implies changing the neutron flux by a 
factor 4.

Example 13.3:

Calculate the typical times of different stages of microstructure evolution and the times to 
steady state for the case of 293 K neutron irradiation of bcc Fe (lattice parameter 2.82 
A) with a dislocation density of \(10^8\) cm\(^{-2}\), and determine if we are in the recombination 
dominated or sink dominated regime \(K\). It is given that the vacancy and interstitial 
migration energies are 1.5 eV and 0.65 eV, respectively, that the recombination number 
is 200, the displacement rate is \(10^{-7}\) dpa/s and the vibration frequency is \(10^{13}\) Hz.

\(k = 10^{-7}\) dpa/s 

\(T = 273 K\)

For bcc Fe, \(Z = 8\) and the elemental jump distance is \(a_0 / 2 = 2.44\) A.

This means that the diffusion coefficient is

\[
D_i = \frac{8}{6} \times (2.44 \times 10^{-8})^2 \times 10^{13} \times \exp(-0.65/8.62 \times 10^{-5} \times 293) = 5.3 \times 10^{14} \text{cm}^2/\text{s}
\]

The vacancy diffusion coefficient is

\[
D_v = \frac{8}{6} \times (2.44 \times 10^{-8})^2 \times 10^{13} \times \exp(-1.5/8.62 \times 10^{-5} \times 293) = 1.27 \times 10^{-28} \text{cm}^2/\text{s}
\]

and the recombination rate constant is

\[
K_{iv} = 200 \times 10^{13} \times \exp(-0.65/8.62 \times 10^{-5} \times 293) = 1.33 \times 10^4 \text{ s}^{-1}
\]

Given the above, the time for recombination to become important is

\[
\tau = \frac{1}{\sqrt{kK_{iv}}} = \frac{1}{\sqrt{10^{-7} \times 1.33 \times 10^4}} = 274 \text{s}
\]
The time for interstitials to arrive at the sinks is

$$\tau_2 = \frac{1}{z_r \rho_c D_i} = \frac{1}{1.02 \times 10^8 \times 5.3 \times 10^{-14}} = 1.86 \times 10^5 \text{ s} = 5.1 \text{ h}$$

The final steady state is reached when vacancies arrive at the sinks

$$\tau_3 = \frac{1}{z_v \rho_c D_v} = \frac{1}{10^8 \times 1.28 \times 10^{-28}} = 7.8 \times 10^{19} \text{ s} = 2.48 \times 10^{12} \text{ years}$$

Since this is longer than the age of the universe, steady state by this mechanism is not reached by this mechanism. In this case, the concentration of vacancies continues to increase until their concentration is so high as to cause defect clustering. See section 13.6.

Close Example 13.3

Sink Dominated Regime

If the defects are very mobile, the sink density high enough or if the displacement rate is low enough, then the recombination can be neglected with respect to absorption at sinks and the equations 13.30 and 13.31 are simplified:

$$\frac{\partial C_v}{\partial \tau} = k - \sum_s K_{sv} C_s C_v \quad (13.50)$$

$$\frac{\partial C_i}{\partial \tau} = k - \sum_s K_{si} C_s C_i \quad (13.51)$$

The steady state solutions of this equation are:

$$C_v = \frac{k}{\sum_s K_{sv} C_s} \quad (13.52)$$

$$C_i = \frac{k}{\sum_s K_{si} C_s} \quad (13.53)$$

This is shown in greater detail in Figure 13.6.
By comparison with Fig. 13.5, the buildup and accumulation of defects is limited by arrival of defects at sinks. That is, characteristic time $t_2$ defined in equation 13.39 is shorter than $t_1$, equation 13.36. When the fast defect (interstitial) starts arriving at the defect sinks, its concentration reaches a quasi steady state, in which the interstitial creation rate is equal to its elimination at the sinks. The interstitial concentration then levels off at a value

$$C_i = k \tau_2 = \frac{k}{\sum_s K_{is} C_s}$$  \hspace{1cm} (13.54)$$

The vacancies continue to increase until time $\tau_3$ when they start arriving at sinks

$$C_v = k \tau_3 = \frac{k}{\sum_s K_{sv} C_s}$$  \hspace{1cm} (13.55)$$

Thus, in the sink-dominated regime, the defect concentrations are linearly proportional to the defect creation rate and inversely proportional to the sink density. In this case also, the equation 13.44 is valid.
Example 13.4: 

Calculate the steady state defect concentrations for high temperature neutron irradiation of zirconium. Assume that $T_{irr}=573$ K, $k=5\times10^{-8}$ dpa/s, $\rho_d = 10^{10}$ cm$^{-2}$, and that the diffusion coefficients pre-exponentials are equal to 0.01 cm$^2$/s. Perform the calculations for $E_m^v = 1.65$ eV and 1.0 eV and $E_m^i = 0.1$ eV and 0.5 eV. Compare with the equilibrium defect concentrations if $E_f^v = 1.5$ eV; $E_f^i = 3.0$ eV. When will steady state be reached?

$D_i = 0.01 \times \exp(-0.1/8.62 \times 10^{-5} \times 573)$ cm$^2$/s and likewise for the other diffusion coefficients.

$C_i = \frac{k}{z_i D_i \rho_d}$ which for 0.1 eV gives $3.7 \times 10^{-15}$ and for 0.5 eV gives $1.2 \times 10^{-11}$

$C_v = \frac{k}{z_v D_v \rho_d}$ which for 1.0 eV gives $3.1 \times 10^{-7}$ and for 1.65 eV gives 0.16

The time for interstitials to arrive at sinks is thus $\tau=1/z_i \rho_d D_i = 7.5 \times 10^{-8}$ s and $2.4 \times 10^{-4}$ s (interstitials arrive essentially instantaneously at sinks) and that for vacancies is $\tau=1/z_v \rho_d D_v = 3.2 \times 10^6$ s and 6.2 s for 1.65 and 1.0 eV migration energy, respectively. It is noteworthy the very large influence of the migration and formation energies of the defects on the defect concentrations, and the large differences between vacancies and interstitials. However the value of 0.16 (16%) for the vacancy concentration is unphysical, as much before such a concentration would be achieved the vacancies would start interacting with each other and forming divacancies which would limit the further increase of the vacancy concentration.

The equilibrium defect concentrations at this temperature are $C_v^{eq} = 6.47 \times 10^{-14}$ and $C_i^{eq} = 4.2 \times 10^{-27}$. As expected the equilibrium defect concentrations are orders of magnitude lower than those seen under irradiation.

An example of a rate theory calculation showing the evolution of defect clusters of different sizes is shown in figure 13.8. This calculation was performed for the parameters shown and is an example of a recombination dominated case in which the controlling process that determines defect concentrations is their arrival at sinks. The idealized curves shown in Figure 13.7 are reasonably well reproduced.

[Figure 13.8 to be inserted]

13.6 Other Models Limitations and possible improvements

Several approximations were made in these derivations, and more sophisticated versions of rate theory modeling take some of these effects into account. There are also other
classes of models for microstructure evolution under irradiation, including the production bias model[7], which takes into account the spatial and temporal correlation of damage production. In the last few years there has been an increase in the use of kinetic Monte Carlo simulations of microstructure evolution[8, 9]. This last method, is for the moment restricted to the description of the early stages of radiation damage and microstructure evolution. Along with other computational methods is bound to increase in importance as computers become more powerful, and can run enough histories to create an average picture of the evolution of microstructure. In the present day, limitations on computer power do not allow an extension of these calculations to the time domains where thermal diffusion can be simulated. We review in the following some of the revisions that can be performed within the framework of the rate theory formulation presented here.

13.6.1. Consideration of Higher Order Clusters

One of the most obvious additions or changes would be the possibility of forming other atomic species, such as vacancy clusters or defects trapped at solute impurities. In this case, additional balances for these other atomic species need to be written and solved simultaneously with the point defect balances, as is done in the case of irradiation induced segregation (chapter 24).

To evaluate the characteristic time for divacancy formation to significantly affect microstructure evolution we set

\[
\frac{\partial C_v}{\partial t} = -K_{vv}C_v^2
\]  

(13.56)

From this we obtain the characteristic time for di-vacancy formation \( \tau_5 \):

\[
\tau_5 = \left[ \frac{K_{vv}}{kK_sC_sK_{vv}} \right]^{1/3}
\]

(13.57)

For example, in example 13.4 above, for interstitial migration energy of 0.5 Ev and vacancy migration energy of 1.0 Ev this time would be 74 s, which means that divacancy formation needs to be considered in that case, as had been inferred by the large vacancy concentrations achieved when this process is neglected.

In general if \( \tau_5 \) is smaller than any of the times \( \tau_1-\tau_4 \) above, then divacancy formation needs to be considered. If the features in the microstructure evolve with time (e.g., sinks are created, their strength varies), then more sophisticated versions of the sink strengths have to be derived.

13.6.2. Solutions of the Spatially Dependent Rate Equations
Another consideration is the spatial dependence of radiation damage. Clearly the mean field approximation does not consider the variation of defect concentration with distance from a sink. Some studies have considered this effect, especially for the case of thin foils under electron irradiation [10, 11].

13.6.3. Displacement Rate

As mentioned before the NRT value given by 12.41 represents the sum total of all defects displaced from their sites, but only a small fraction of these survive. The quantity taken for $k$ then depends on the effect we want to evaluate. If it is an effect such as irradiation creep or void swelling that depends on the long-range migration of point defects, then the appropriate quantity to use is the rate of generation of freely migrating defects. This is given by

\[ k = \eta k_{NRT}, \]  

where $\eta$ is the efficiency of freely migrating defect production. This efficiency is on the order of 0.01-0.05 for neutron and heavy ion irradiation, about 30% for proton irradiation and 100% for electron irradiation. Formulas relating this efficiency with the average recoil energy are given in [12].

Another limitation not taken into account in the formulation above is that as defects accumulate, the space available for the creation of new defects decreases. In that case there would be a correction given by

\[ k = \eta k_{NRT} (1-(C_i+C_v)) \]  

In most cases these corrections are small, as defect concentrations are lower than $10^{-4}$.

Unlike the corrections mentioned above, the corrections to the production rate do not change the general form either of the equations or of the solutions.
Problems

1. Solve the equations below to obtain the steady-state vacancy and interstitial concentrations for the case of absorption of defects at dislocations and at voids

\[
\frac{\partial C_v}{\partial t} = k - K_v C_v C_v - z_v \rho_d D_v C_v - 4\pi r_c N D_v C_v
\]

\[
\frac{\partial C_i}{\partial t} = k - K_v C_v C_v - z_i \rho_d D_i C_i - 4\pi r_c N D_i C_i
\]

2. An iron component in a nuclear reactor core is subjected to a fast flux of \(5 \times 10^{13}\) neutrons.cm\(^{-2}\).s\(^{-1}\) at an average energy 1 MeV. The defects created are eliminated only by recombination and by absorption at dislocations. The dislocation density is constant at \(\rho_d = 10^{10}\) cm\(^{-2}\), the interstitial migration energy is 0.5 eV and the vacancy migration energy is 1 eV.

   a. Calculate the interstitial and vacancy concentrations at steady state.
   b. Find the time to reach steady state.
   c. Compare these with electron irradiation at room temperature. Take the \(k_{el} = 5 \times 10^{-3}\) dpa.s\(^{-1}\), and assume an infinite medium similar to the above.

   Make reasonable estimates of any needed parameters.

3. Self-diffusion in U metal occurs by a vacancy mechanism. The diffusion coefficient is \(D = D_0 \exp(-E_{mv}/kT)\) where \(E_{mv}\) is the vacancy migration energy in u.

   a. What is the self-diffusion coefficient of U in the absence of irradiation?
   The formation energy of vacancies is \(E_{fv}\).
   b. During irradiation Frenkel pairs are created at a rate \(k\) (dpa/s), and only destroyed by recombination. What is the steady state vacancy concentration? What is the uranium self-diffusion coefficient by a vacancy mechanism under irradiation?

   c. The interstitial migration energy is \(E_i\). Sketch the variation of \(\ln D_u\) vs. \(1/T\), identifying significant portions of the curve.

4. A thin foil thickness \(L\) is under irradiation. It is desired to calculate the strength of the surface sink. Assume that at the midplane of the foil the concentration is equal to the bulk concentration of defects \(C_{\text{bulk}}\).
If the interstitial diffusion coefficient is $D_i$ solve the diffusion equation for the plate geometry and obtain the flux of interstitials to the surface and identify the rate constant for annihilation of defects at the surface $K_{\text{disl-i}}$ and $K_{\text{disl-v}}$. Neglect defect generation.

5. In section 13.3 we calculated the rate of divacancy formation by considering the reaction of two vacancies in the fcc lattice.

$$v + v \xleftarrow{k^{\text{fcc}}} 2v$$

In that calculation we multiplied the number of configurations from which the reaction can occur by the jump probability. Repeat the calculation for the hexagonal close-packed lattice, that is calculate $K^{\text{hcp}}_{2v}$. Assume that vacancy diffusion occurs between nearest-neighbors in the hcp structure. The vacancy migration energy is $E^v_m$ and the vibration frequency is $\nu$.

6. The reaction rates for reactions between defects and extended sinks were found in this chapter by solving the appropriate diffusion equation. It is also possible to derive these reaction rates by considering a certain fraction of the sites in the solid will be at the surface of extended sinks and that these sites are accessible via other NN sites similar to what was done in the divacancy derivation section 13.4.

a) Derive the dislocation reaction rate using this method and compare to equations 13.%%. Can you explain the differences?

b) Derive the void reaction rate using this method and compare to equations 13.%%. Can you explain the differences?
References


