2055-12

Joint ICTP/IAEA School on Physics and Technology of Fast Reactors Systems

9 - 20 November 2009

Radiation Damage of Structural Materials

for Fast reactor Fuel Assembly (1)

B. Raj & M. Vijayalakshmi
Indira Gandhi Centre for Atomic Research
India

RADIATION DAMAGE OF STRUCTURAL MATERIALS FOR FAST REACTOR FUEL ASSEMBLY

(ICTP/IAEA course, 9-20, November, 09, Trieste, Italy.)

BALDEV RAJ & M.VIJAYALAKSHMI

CONTENTS

PREFACE

PREFACE

Nuclear power can be generated using two types of nuclear reactions (see Figure): the fission and the fusion. In the fission reaction, the nucleus of a heavy atom like uranium (U^{235} or U^{233}) or plutonium (Pu^{239}) is split into lighter fragments, releasing a large amount of energy (~200MeV per fission event). In fusion, on the other hand, nuclei of smaller atoms like isotopes of hydrogen are fused into larger nucleus like that of helium, producing energy (${}_1D^2 + {}_1T^3 \rightarrow {}_2He^4 + {}_0n^1 + 17.6$ MeV).

Nuclear power offers the advantages of environmental friendly and sustainability. The high heat value of fuel, relative high energy density and possibility of high conversion efficiency are some of the additional advantages of nuclear power. Currently, there are 443 commercial fission based nuclear reactors, which account for about 15% of global electric power generation. Newer reactor concepts are emerging in the nuclear industry to meet the growing demands like the cost effectiveness, waste management, improved safety and proliferation resistance. Materials behaviour is the major challenge in bridging the gap between concept to reality.

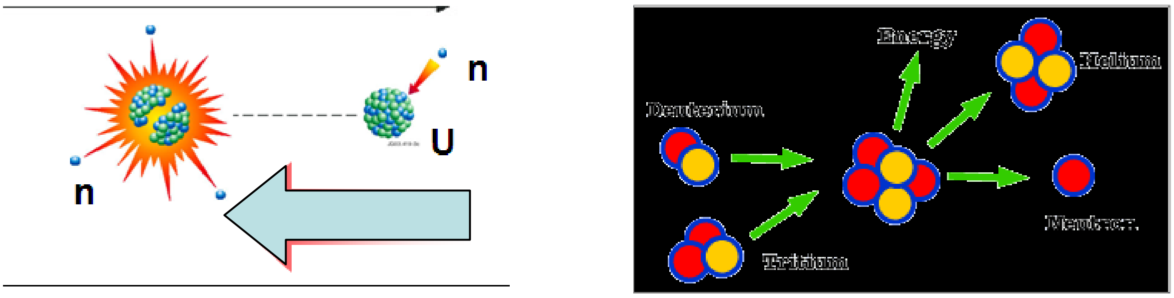


Figure: A typical fission reaction inside a heavy nucleus and fusion reaction between two light nuclei.

Based on energy of the neutrons used for fission of the nuclear fuel, reactors can be broadly classified into two types: ‘thermal’ and ‘fast’ reactors. Materials used in thermal reactors (where fission is caused by neutrons with energies < 1 eV) experience relatively less aggressive conditions. The materials used in fast reactors (where fission is caused by “fast” neutrons with energy of the order of 1 MeV) are exposed to more hostile environment, such as high neutron flux (peak flux: ~ 8 x 10 ^{15} n/cm^2/s against 10^{15} n/cm^2/s in thermal reactors) and high temperatures (up to 823 K as compared to 573 K in thermal reactors). In addition, fuels used in fast reactors are irradiated to much higher levels of burn-up (target burn up* of 200GWd/t; present level of burn-up 100 GWd/t) as compared to the fuels in thermal reactors (up to 80GWd/t). The above features suggest that development of radiation resistant materials are absolutely essential to develop cost-competitive nuclear power.

There are two types of primary damage mechanisms during irradiation: transmutation and displacement damage. In a fission reaction, high energy neutrons are emitted in the fuel of the core of a nuclear reactor, which is roughly 3 neutrons per fission event. These high energy neutrons can travel unimpeded through most of the known materials, other than materials containing lead, boron and cadmium, which are strong absorbers of neutrons. While these neutrons travel through the engineering materials in the reactor, they cause two types of damage: transmutation nuclear reactions and displacement damage. Transmutation reactions refer to the conversion or transmutation of one chemical element or isotope into another, through a nuclear reaction. The second type of damage, namely, the displacement reactions, the major concern of the present course, refer to the physical and mechanical changes caused by the impinging high energy neutron, to the parent lattice due to the ballistic effects of collision.

Presently, there is a global attempt to introduce advanced reactor design concepts, to ensure better thermal efficiency, cost, safety, waste management and proliferation resistance. The nuclear materials play a pivotal role to ensure successful implementation of these concepts. Hence, understanding the behaviour of materials under extreme service conditions of a nuclear reactor, is of paramount importance to develop superior radiation resistant materials.

CHAPTER 1: INTRODUCTION

STRUCTURAL MATERIALS AND THEIR BEHAVIOUR IN A FAST REACTOR FUEL ASSEMBLY

CHAPTER 1: INTRODUCTION

STRUCTURAL MATERIALS AND THEIR BEHAVIOUR IN A FAST REACTOR FUEL ASSEMBLY

One of the main future targets of a nuclear industry is cost-competitiveness. The engineering structural materials in a nuclear reactor contribute to roughly around 15% of the cost of the reactor. Hence, there is a large scope for reducing the cost of the reactor by developing the cost-efficient structural materials in a fast reactor fuel assembly. Towards this goal, certain directions are identified:

(1) develop high burn-up materials;
(2) increase in lifetime from 60 years to 100 years and
(3) materials compatible with coolants operating at higher temperature.

An in-depth understanding of the materials behaviour under service conditions is essential to achieve the above goals.

The service conditions, i.e., the stress, irradiation dose, temperature and environment to which a material is exposed in a fast reactor fuel assembly, changes from component to component. Hence, it is necessary to define what we mean by ‘structural materials’ in a fast reactor fuel assembly, before we proceed to radiation damage in these materials. The first part of the chapter emphasizes the need to distinguish broadly the different circuits in a fast reactor and defines the term ‘structural materials’ in a fast reactor fuel assembly.

CLASSIFICATION OF ENGINEERING MATERIALS IN A REACTOR:

The term ‘nuclear materials’ refers to a host of engineering materials which are used in the reactor, other than fuel, coolant and moderator. The entire reactor systems can be grouped into three major regions or circuits: core, out-of-core and balance of plant (Figure.1.).The nuclear materials can broadly be grouped into two categories: core and out-of-core component materials. The engineering materials in the balance-of-plant are similar to conventional power systems.

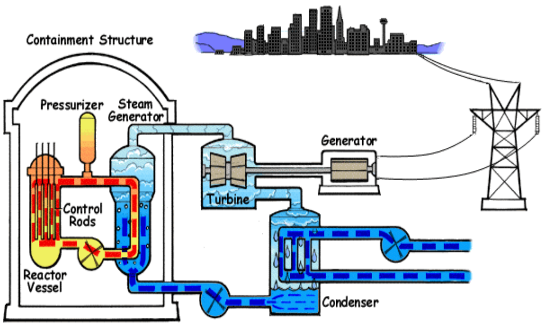


Figure.1. Schematic to represent components in core (red), out-of-core(blue) and balance of plant (black) circuits in a reactor.

The core component materials include the following: fuel assemblies and the neighboring coolant channels for water reactors; and clad (cylindrical tubes which houses the fuel pellets) for the fuel and wrapper (a container which houses fuel elements, in between which the coolant flows) for sub-assemblies of fast reactors. The structural materials include those which are within the core other than clad and wrapper and hence, do not belong to the ‘conventional’ part of the power generation unit. The out-of-core materials, made of different forms of steels form the remaining part of nuclear steam supply system.

CORE COMPONENT MATERIALS:

Conventionally, in a fast reactor systems, the materials that constitute the clad and the wrapper are the major components of the fuel sub assembly or the core. These are referred to as ‘core component materials’. The necessity to develop these materials arises from the fact that the “burn-up” of the fuel, depends on the performance of the clad materials. The development of robust materials technology to achieve high burn-up (energy production from unit quantity of the fuel) of the fuel is an important step towards reducing the cost of nuclear energy production. The higher burn up of the fuel, increases the ‘residence time’ of the sub assembly in the core and thus lowering the cost. Figure. 2 shows the dependence of the burn up on the residence time, based on Russian experience.

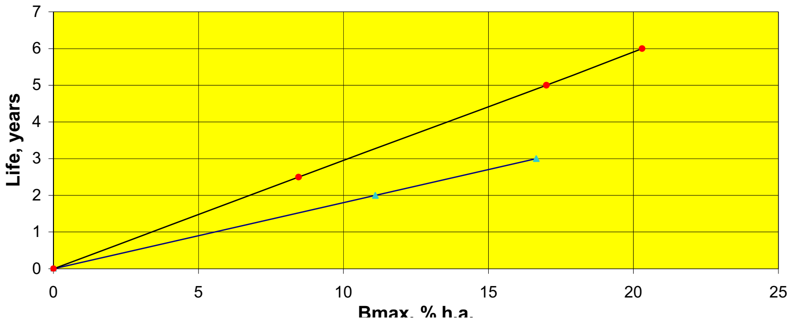


Figure.2. Dependence of residence time on burn up of fuel, for different fuel element diameter. Blue dots : BNH 600 fuel element diameter-6.9 mm & maximum linear heat rate – 47.5 kW/m; Red dots: BN-K fuel element diameter- 9.5 mm & maximum linear heat rate – 45 kW/m.

The fuel sub-assembly consists of hexagonal array of wrappers which contains the clad tubes, as shown in figure.3. The clad materials in fast breeder reactors are exposed to severe environmental service conditions, as shown in Table.1.

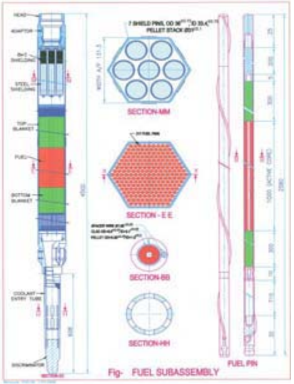


Figure.3. Schematic of the clad, wrapper and fuel sub-assembly in the core of a fast reactor.

Properties	Criterion
Radiation environment	Severe radiation environment leads to material problems - Fast neutron flux: 10^{20} n/m^2/s - Fluence : 2 x 10^{27} n/m^2 Achievable burnup limited by material degradation
Compatibility with Fuel pin	Fission gas in fuel pins - increase in internal pressure Provide plenum space of sufficient volume Internal corrosion of cladding due to volatile fission products - Lanthanides series fission products
Compatibility with sodium	Operation in hot sodium - Corrosion/erosion of structural materials Appropriate control of sodium chemistry
Radiation damage	Irradiation induced changes in structural material properties - Significant dimensional & mechanical property changes - Severe radiation environment leads to material problems like Void swelling, Irradiation creep & Helium embrittlement

Table 1. Service exposure conditions for clad materials in a fast reactor core.

Given the above environmental or operating conditions of a fast reactor, it is necessary to evaluate the severity of these conditions component by component. For example, the clad tube which contains the fuel, experiences more aggressive environment than the wrapper which houses a large number of clad tubes. Table.2. provides the difference in the exposure condition of the clad and wrapper in a fast reactor core.

The accumulated experience in fast reactor technology is mainly from sodium cooled reactors, in a few countries like France, Japan, UK, USA, Russia and India. Two types of materials, the Stainless Steels (SS) and the nickel-iron based alloys, were evaluated in 1970's for core applications, based on their excellent high temperature mechanical properties. Subsequent efforts focused on stainless steels, since nickel based alloys under irradiation exhibited high tendency for helium embrittlement. Three generations of steels have been developed : variants of austenitic Stainless Steel (SS) like 316 SS and D9 (Ti modified 15Ni-15Cr austenitic steels), the 9-12 Cr based ferritic steels and the Oxide Dispersion Strengthened (ODS) advanced ferritic steels.

Criterion	Clad Tube	Wrapper Tube
Irradiation effects	Void swelling Irradiation creep Irradiation embrittlement	Void swelling Irradiation creep Irradiation embrittlement
Mechanical properties	Tensile strength Tensile ductility Creep strength Creep ductility	Tensile strength Tensile ductility
Corrosion	Compatibility with sodium Compatibility with fuel Compatibility with fission products	Compatibility with sodium
Good workability		
International irradiation experience as driver or experimental fuel subassembly		
Availability		

Table.2. Difference in the selection criteria of clad and wrapper in a fast reactor fuel assembly

STRUCTURAL MATERIALS:

Apart from the above crucial components like the fuel sub-assemblies, there are many components in the core. These include core support structures, main vessel, inner vessel, intermediate heat exchangers, near core components like the grid plate, to mention a few. The operating conditions of these components are not as severe as the fuel sub-assemblies, clad and wrapper. The operating temperatures, temperature gradients, irradiation levels and sodium interaction are all less. However, these are permanent structures of the reactors, expected to serve for about the life of the reactor, which nowadays is expected to reach 100 years. The materials of these components called as ‘structural materials’ are normally different types of special steels. The major selection criteria of structural steels are shown in Table.3.

The materials for out-of-core and balance of plant circuits will not be discussed in this chapter. The core component materials, clad and wrapper, alone will be discussed.

With the above introduction to the definition of different types of engineering materials in a fast reactor fuel assembly, the next part of the chapter would focus on introducing the basics of radiation damage.

Properties	**Criterion**
Mechanical	High mechanical properties - creep - low cycle fatigue - creep-fatigue interaction - high cycle fatigue
Sodium environment	Compatibility with liquid sodium
Structural stability	
Availability of design data (RCC-MR/ASME design codes)	
Weldability, Workability	
International experience	
Cost	

Table 3. Criteria for selection of Reactor Structural Materials

BEHAVIOUR OF CORE COMPONENT MATERIAL:

Materials in the fast reactor fuel assemblies exhibit many phenomena, as described below:

In a fast reactor core, the materials can change its shape and volume by tens of percentages, increase hardness by factors of five or more, reduce ductility and increase embrittlement. To give an example, it is possible for a cube of nickel to increase its side from 1 cm to 1.06 cm, after an exposure to irradiation of 10^{22} n/cm^2. This is nearly 20 % isotropic increase in volume due to a process called 'void swelling' !!

Another feature is the 'irradiation growth'. A cylindrical rod of uranium, say 10 cm long 1 cm in diameter, (volume - 7.85 cm^3) irradiated to a flunce of 10^{20} n/cm^2, can increase its length three times, 30 cm and reduce its diameter to 0.58 cm, retaining the volume same as 7.85 cm^3. The irradiation growth, anisotropic in nature, introduces severe distortion in core components.

The third feature is the irradiation hardening. Exposure of metals under irradiation at temperatures < 0.3 Tm, changes the stress- strain behaviour significantly. The yield strength of the material increases, concomitant with the significant reduction in ductility. These changes are introduced by the steady state defect microstructure of the material under irradiation.

Irradiation creep, the most important parameter for design consideration is the augmentation of thermal creep of the material, under irradiation. This leads to premature failure of the material and restricts the service life. The mechanisms that contribute to reduction in creep life are related to the interaction of point defects with line and planar defects in the material.

Irradiation embrittlement, another frequent observation in materials exposed to irradiation, refers to the increase in the 'Ductile to Brittle Transition Temperature (DBTT)' during irradiation. In certain materials, this phenomenon makes the material highly brittle at room temperature that the post-irradiation handling of core component materials become difficult. Some of the engineering materials contain nickel, an element which undergoes (n,α) reaction, producing high concentration of helium. The helium stabilized irradiation induced voids and form along the grain boundaries weakening the materials causes embrittlement called the ‘helium embrittlement’.

The damage mechanisms operating in a material under irradiation in a fast reactor fuel assembly can be summarized as follows:

(1) Void Swelling

(2) Irradiation Growth

(3) Irradiation Hardening

(4) Irradiation Creep

(5) Irradiation Embrittlement and

(6) Helium Embrittlement.

All the above degradation mechanisms are related directly to the production, diffusion and interaction of point defects in the material. Hence it is essential to understand the key features of point defects before proceeding to the degradation mechanisms.

BASICS OF POINT DEFECTS:

We know that the atoms in a crystalline lattice occupy their equilibrium positions, under normal circumstances, as shown in Figure.4.

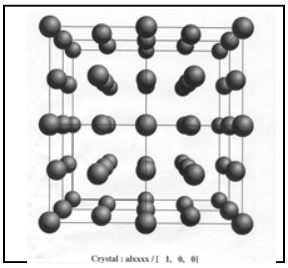


Figure.4. Periodic arrangement of atoms in a crystalline ‘host’ lattice.

When a stream of high energy neutrons ‘bombard’ this lattice, the atoms are ‘knocked off’ from their equilibrium locations. For the sake of simplicity, let us assume that only one high energy neutron, or in a general case, a particle is impinging on one lattice atom. The amount of energy transferred by the incident particle to the host lattice atom is related to the masses (m) of the incident particle, the host lattice atom and the incident energy (E_0) or the velocity of the incident particle, the velocity, if any, of the host lattice atom. Based on conservation of kinetic energy before and after collision, the energy transferred to the host lattice atom can be shown to be

$$E = E_0\, 4\{(m_1 x\, m_2)/\, [m_1 + m_2]^2\} \qquad \text{..... 1.1}$$

Usually in crystalline lattices, the energy required to 'knock off' an atom from its equilibrium position is of the order of few tens of eV's. For example, the 'displacement energy' in a lattice of copper near melting point is around 35-40 eV. The remaining energy which is transferred by the incident neutron manifests as kinetic energy of the host lattice atom. Thus, the collision of the first neutron with a lattice atom leaves behind another host lattice atom, with kinetic energy, sufficiently high enough to 'knock off' another lattice atom, by the same process of collision. The only difference is that the energy transferred by the projectile of host atom to another static lattice atom is far higher, since mass of an impinging atom is order of magnitude more than neutron. This process repeats till the mobile atoms have transferred all their kinetic energy and have come to rest or 'relax' in available locations, which need not be lattice site. The process is called the 'displacement cascade'. The first atom which gets knocked off is called the primary knock on atom (PKA) and the subsequent displaced atoms are called the secondary, tertiary knock-on atoms respectively (Figure.5.).

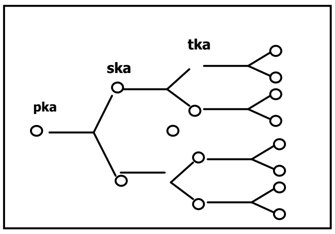


Figure5. Generation of primary knock on atom by the impingement of energetic incident neutron, followed by creation of secondary and tertiary knock on atoms in subsequent collisions.

How many lattice atom displacements will occur if a neutron of energy Ei strikes a lattice atom ?

The answer to this question will enable us to quantify the displacement damage. It is basically required to find out the no of atoms displaced by a PKA of energy E. It is done as follows:

To quantify displacement damage, it is necessary to set up the damage rate equation and solve. A brief approach is given below:

The displacement rate can be written as

$$R_d = N \int \phi (E_i) \sigma_D (E_i) dE_i \qquad ..... 1.2$$

wherein N is the density of lattice atoms, ϕ the energy dependent particle flux and σ_D the displacement cross-section.

$$\sigma_D (E_i) = \int \sigma (E_i , T) \gamma (T) dT \qquad ..... 1.3$$

where $\sigma (E_i , T)$ is the probability that particle of energy E_i imparts recoil energy to a struck lattice atom and γ is the parameter to be evaluated, namely number of displaced displacements during collision. While solving these equations using appropriate models, it is possible to show that

$$\gamma (T) = 0 \text{ if } E_t < E_d \qquad ..... 1.4$$

1 if $E_d < E_t < 2 E_d$,

$E_t/2E_d$ if $2E_d < E_t < E_c$

$E_c/2E_d$ for $E_t >> E_c$.

The resulting behaviour can be summarised as shown in figure.6.

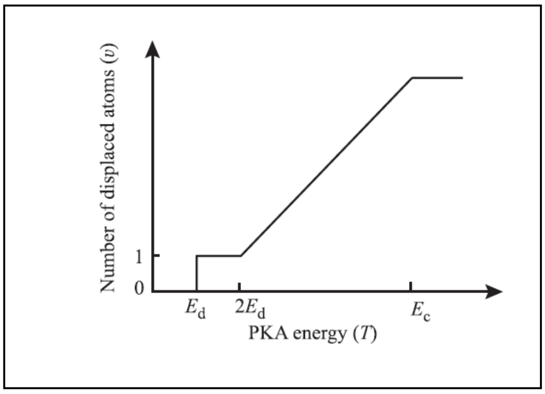


Figure.6. Variation of number of displacements in a lattice with the energy of the primary knock on atom(PKA).

If the energy of the PKA is less than the displacement energy of around 20-40 eV in most metals, no atom is displaced. The small energy that is transferred manifests as increased vibration of the lattice atom about its mean equilibrium position and hence as 'heat'. When the energy transferred is between E_d and $2E_d$, two possibilities emerge: the struck atom gets displaced and the PKA with energy $< E_d$, jumps back into the lattice site. Or if the original PKA does not transfer E_d, there is no displacement. Either way, there can only be one displacement possible. The number of displacements can range from 0 to $E_f/E_d - 1$, and for large E_f, no of displacements reach E_f/E_d. The displacement function is given by the above function and the behaviour is depicted in figure.6. For most metals, the value of E_d is around 20 or 40 or 90 eV.

There are four major stages in which the cascade evolves during irradiation:

1. Collisional
2. Thermal Spike

3. Quenching
4. Annealing.

In the collisional stage, the primary recoil atom initiates a series of displacive collisions that continues till no atom has enough energy to displace any more atom. This stage lasts for about 1 ps. At the end of this stage, the lattice ends up with energetic displaced atoms and vacant lattice sites. This time is not sufficient for the formation of stable lattice defects.

In the second stage, the 'thermal spike', lasting for another ps., the collisional energy of the displaced atoms is shared amongst the neighbouring atoms. This leads to formation of a region of high energy density leading to a spike of about 1ps., and the position of atoms in the spike region would resemble that of molten metal.

As there is a continuous, simultaneous transfer of energy to the adjacent atoms, the spiked region gets quenched or relaxed, in about 10 ps., leading to a stage close to thermodynamic equilibrium. Stable lattice defects like point defects or the defect clusters like loops form during this stage.

The annealing stage, as the name suggests is a thermally activated process. Further rearrangement of defects occur by thermal diffusion of mobile lattice defects. This is a stage which depends on the irradiation condition, temperature, and defect kinetics with the matrix.

The above processes lead to the creation of large number of vacant lattice sites (since many atoms are 'knocked off' from their equilibrium sites), called the 'vacancies' and host atoms coming to 'halt' at sites, which are not equilibrium lattice sites, called the 'interstitials'. Normally, the concentration of vacancies produced during irradiation at room temperature is ~ 10^{-2}, which is two orders of magnitude higher than thermal equilibrium concentration of vacancies near melting point of say, copper ~ 10 $^{-4}$. The core of a displacement cascade is rich with vacancies and peripheral area with interstitials. A typical disorder introduced in a perfect lattice in a displacement cascade is shown in figure.7. These defects, the vacancies and the interstitials, are called the point defects.

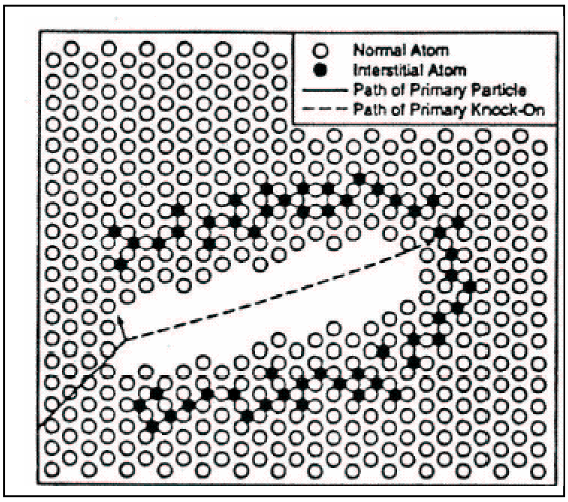


Figure.7. Atom position at the end of a single 'displacement cascade' showing the vacancy rich core and the interstitial rich peripheral regions.

The different stages and the time domains in which these stages proceed are shown in Table 4.

Time (s)	Event	Result
10^{-18}	Energy transfer from incident pcle	Primary Knock On generated
10^{-13}	Displacement of lattice atoms by PKO	Displacement cascade
10^{-11}	Energy dissipation, spontaneous recombination & clustering	Stable Frenkel pairs & defect clusters
10^{-8}	Defect reactions by thermal migration	Single interstitial atom & vacancy recombination, clustering, trapping & defect emission

Table.4. Different stages of defect evolution during irradiation

The defects that are finally introduced in a crystalline lattice during irradiation are

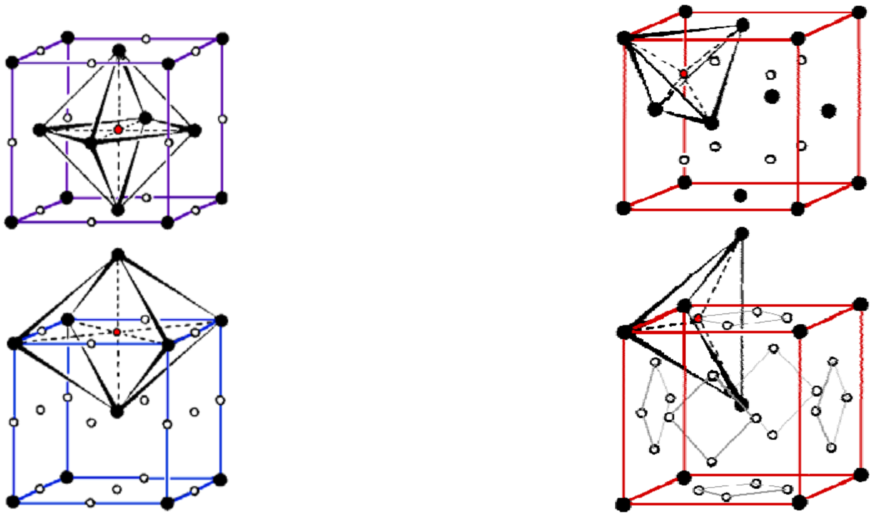
- Ponit Defects (0 D) : vacancies and interstitials

- Line Defects – (1D) : dislocation lines
- Planar Defects – (2D) : dislocation loops
- Volume Defects (3D) : voids, bubbles,

Point defects are the basic entity. The concentration and diffusion characteristics of point defects determine the changes in physical and mechanical properties of materials.

Point Defects:

Interstitial: An interstitial is an atom which occupies a position in a crystal lattice, which does not belong to regular lattice site. There are two types of interstitial sites: Octahedral and tetrahedral. Octahedral sites are interstitial positions that are surrounded by an octahedron, whose six vertices are occupied by lattice atoms. Similarly, the tetrahedral sites are interstitial positions that are surrounded by a tetrahedron, whose four vertices are occupied by the lattice atoms. Figure.8. shows the octahedral and tetrahedral sites in a fcc and bcc lattice.



Octahedral *Tetrahedral*

Figure.8. Octahedral(left) and tetrahedral(right) sites in fcc and bcc lattices.

This is too simple a picture of an interstitials. Most often, two Self Interstitial Atoms (SIA's) share a single interstitial site, forming a dumb-bell. The formation of such dumb-bells displace the atoms around them from their equilibrium lattice site, resulting in an elastic displacement field around the interstitial. The total amount of distortion of the original lattice due to the formation of such interstitials or dumb-bells is called the 'relaxation volume'. The value of the relaxation volume for interstitials in metal lattices range from 1 to 2 atomic volume. The high distortion or the elastic interaction around interstitials is responsible for the interstitials to attract mobile SIAs. It is difficult to form interstitials, as clear from the high formation energy of around 2 to 3 eV in most metals. This leads to very low equilibrium concentration of interstitials near melting point, $\sim 10^{-18}$ to 10^{-6}. Interstitials are highly mobile, with the migration energy of around < 0.1 eV. The interstitials have high binding energy of around 1 eV. Hence, it is difficult to dissociate large interstitial clusters, at low temperatures.

Vacancies:

The vacancy or a missing lattice atom is the simplest defect in a lattice. Vacancies, unlike interstitials, have low formation energy (~1-2 eV), low relaxation volume (0.1 to 0.5 atomic volume) and high migration energy (> 0.5 eV). Hence, vacancies are less mobile than SIA's. Multiple vacancies have less binding energy (0.1eV) and hence vacancy clusters are less stable than clusters of SIA's. Vacancies can bind to oversize solute or an oversize impurity atom (0.2 to 1 eV), to lower the overall free energy of the system.

Unlike interstitials, vacancies are thermodynamically stable defects, as is shown below. Even in a perfect crystal, in the absence of irradiation, presence of vacancies is thermodynamically desirable. It is possible to show that the free energy of a crystal, F is reduced with vacancies.

$$F \sim G = U + pV - TS = H - TS \qquad \ldots\ldots 1.5$$

Where F is the free energy of the crystal of volume V at constant pressure, p at temperature T, U the internal energy, S the entropy and H the enthalpy of N atoms constituting the system.

$$\nabla S_{mix} = k \ln \omega \qquad \text{..... 1.6}$$

where ω is the number of possible configurations.

Consider the introduction of ‘n’ defects with N available sites in the crystal. The increase in free energy is

$$\nabla G_f = n \nabla H_f - T \nabla S \qquad \text{..... 1.7}$$

∇H_f is the increase in the internal energy due to introduction of defects and ∇S is the corresponding increase in entropy. It can be shown that

$$w = \{ [N (N-1) (N-2)....(N-n+1)] / n !\} \qquad \text{..... 1.8}$$

∇Smix is calculated using the expression for ω in the equation for ∇Smix. The introduction of defects introduce vibrational disorder, which can be calculated and finally the total ∇S, by adding both contributions.

In equilibrium n will be such that $dG_f/dn = 0$. This condition can be used in the equation for dG_f to arrive finally at the concentration of ‘defects’ as follows:

$$C = n / N = \exp (-\nabla G_f / kT) \qquad \text{..... 1.9}$$

The above general equation, can be now re-written for the two types of point defects, to get an expression for concentration of the point defects.

For vacancies,

$$C_v = \exp (-E^f_v /kT) \text{ X } \exp (S^f_v / k) \qquad \text{..... 1.10}$$

$$C_i = \exp (-E^f_i /kT) \text{ X } \exp (S^f_i / k) \qquad \text{..... 1.11}$$

Where the subscript f refers to formation term and v and i refer to vacancies and interstitials. ($E^f = \nabla H^f$,). It requires much less energy to form vacancies than interstitials, (E^f_v=<1eV and E^f_i = ~ 4 eV), $C_v >>> C_i$, when the system is at thermal equilibrium.

The diffusion of these defects, through the lattice occurs at different rates by various mechanisms.

Defect Dynamics in a Crystal under Irradiation:

When the crystal is subjected to irradiation, it is already shown that Frenkel pairs (pair of vacancy, V and interstitial, I) are produced whose concentration is two orders of magnitude more than that in thermal equilibrium. These defects are either lost through recombination of vacancies and interstitials or to the sinks like loops, voids. Thus, the local concentration of defects, either vacancies or interstitials, is a balance between

(1) local production rate, (2) reaction with other defect species and (3) diffusion into or out of the region of interest. The main defect reactions considered are

$$V + I \dashrightarrow \qquad \text{….. 1.12}$$

Where,□ is a lattice site. Point defect reactions with sinks, s, are written as

$$V + s \dashrightarrow s \;\text{ or }\; I + s \dashrightarrow s \qquad \text{….. 1.13}$$

The chemical rate equations are established, based on the production rate of defects, their recombinations rate and the rate of loss of defects at various types of sinks:

$$dC_v / dt = K_o - K_{iv}\, C_i\, C_v - K_{vs}\, C_v\, C_s \qquad \text{….. 1.14}$$

$$dC_i / dt = K_o - K_{iv}\, C_i\, C_v - K_{is}\, C_i\, C_s, \qquad \text{….. 1.15}$$

where C represents the concentration of either vacancy, v or interstitial i or sink, s and K's represent the rates of either production K_o or K_{iv} or K_{is} the reaction rate between vacancy and interstitial or interstial/vacancy and sink. The build up of point defects depends on the various factors listed above. Based on rate theory calculations, it can be shown that initially at small times,

$$dC/dt = K_o, \text{ with } C_i = C_v = C = K_o t.$$

The build up of point defects will start leveling off when the production rate of the defects is offset by their recombination rate. Eventually, the interstitials(first) and then the vacancies(later) will begin to find the sinks and one enters the “sink dominated regime”. The concentration of free point defects is dictated by the rate of loss of point defects to sinks. Since $D_i >> D_v$, more interstitials are lost to sinks than vacancies. The interstitals will decay faster and the build up of vacancies occur. Hence, $C_i <<< C_v$. After a while, decided by the time constant for the slowest process, the true steady state is achieved, wherein the vacancies are lost by interaction with the sinks. Thus, the concentration of vacancies and interstitials, though equal in the beginning, decided by the production rate, change with time as they evolve, depending upon their recombination rates, mobility and loss to sinks. The exact nature of the evolution is very sensitive to energy terms, mobility values and sink density and their strength. Figure. 9. shows a typical behaviour of variation of point defects for low sink density at low temperature.

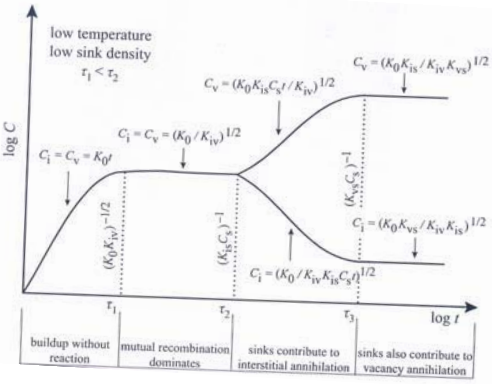


Figure.9. Variation of concentration of vacancies and interstitials with time at low temperatures with low sink density.

It is possible to solve the above equations to arrive at the time evolution of each type of defects, namely concentration of vacancy or interstitial, for different combination of temperature and sink densities.

CLUSTERING OF POINT DEFECTS:

The two types of point defects, vacancies and interstitials, are generally produced in equal numbers. Hence, most of them undergo ‘recombination’ process, which means that a host lattice atom in the non-lattice site jumps back to a lattice site, restoring the atomic configuration in the original lattice. But this process does not reach completion, leaving behind some fraction of mobile vacancies and interstitials.

The defects explained above finally rearrange themselves into other defect configurations. One of these configurations is the two dimensional dislocation loops. These ‘loops’ can either be of interstitial type or the vacancy type, which means that they can be formed by the condensations of excess vacancies or interstitials. A schematic of lattice planes of a crystal, in which these loops are formed, is shown in figure.10, along with transmission electron micrographs of the loops, which enable us to identify the type of the loop.

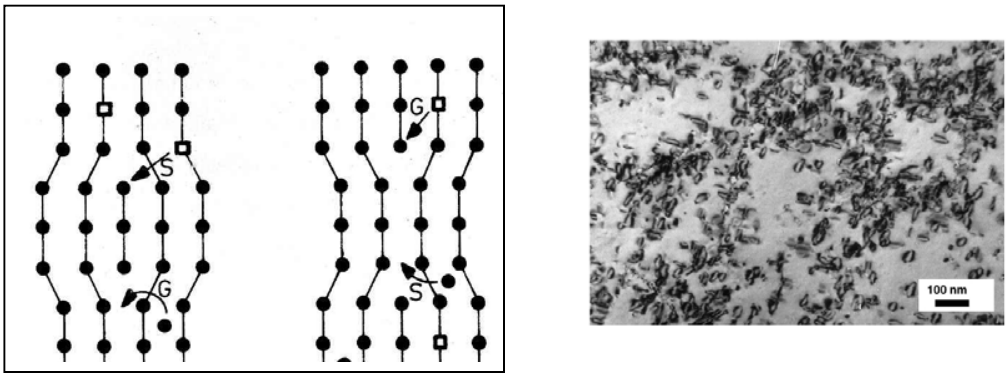


Figure.10. Schematic of an interstitial and a vacancy loop and rearrangement of the adjacent lattice planes. TEM micrograph shows the dislocation loops, which when analysed can be identified as either vacancy or interstitial loops. G and S represent the preferred direction for adsorption of vacancy and interstitial.

INFLUENCE OF POINT DEFECTS IN MICROCHEMISTRY OF THE LATTICE:

One of the consequences of interaction of point defects with defects and solutes in the material is to introduce inhomogeneity in the chemical composition of the lattice. This phenomenon called the “radiation induced or enhanced segregation”, which will be briefly discussed below.

Consider an alloy of A-50%B, in which vacancies and interstitials are produced by irradiation. Since the grain boundaries are strong sinks for point defects, both the defects flow towards grain boundaries. Let us consider, for a moment, only the flux of vacancies. Initially, irradiation had produced vacancies, uniformly distributed in the lattice. Hence, the concentration of vacancies remained the same everywhere. However, once sinks like grain boundaries were introduced, there is a preferential flow of vacancies towards grain boundaries. Consequently, the concentration of vacancies change near the grain boundary, as shown in the figure. 11. The flux of vacancies towards sinks, i.e., grain boundary is balanced by an equal flux of atoms in opposite direction. But the A and B atoms are not likely to participate in this flux equally, since they bind with vacancies with different energies and the mobility of A atom by vacancy mechanism and that of B atom by vacancy mechanism do not remain the same. Let us assume that A atoms participate in the vacancy flux more than B atoms, there is a net loss of A atoms to the boundary and a relative gain of B atoms. This process changes the composition of the regions near the grain boundary to be the one rich in A and depleted in B, leading to concentration gradient, in an originally homogeneous alloy. Similar arguments can be extended for interstitials also.

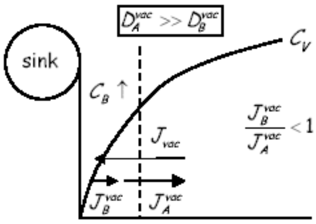


Figure.11. Radiation induced segregation altering the original composition of the alloy near strong sinks like grain boundaries.

Whether an atom A enriches or depletes near a sink, when both the processes operate, depends on the relative stability of an atom associated with the particular defect flux. The type of atoms which diffuse to different sinks depends on the size of the atom, its mobility and binding energies.

For example, the undersized solute elements like Ni, Si and P, which are present in austenitic stainless steel, move towards neutral sinks like grain boundaries and interfaces between precipitates and austenite matrix, while oversized elements like Cr, Mo and Nb show depletion around these sinks. Nickel and silicon get enriched near biased sinks like dislocations also, while titanium, molybdenum and chromium move away from such biased sinks. It is also observed that the segregation is less for mobile dislocations and more for conservative Frank loops.

INVERSE KIRKENDALL EFFECT :

In general, in a binary alloy AB, the vacancy flux J_V towards the sink S gives rise to atom fluxes J_A and J_B in opposite directions ($J_V = J_A + J_B$). The atomic fluxes, J_A and J_B will be proportional to the concentrations C_A and C_B of the alloy and their diffusion coefficients D_A and D_B. There will be no change in the alloy composition near the sink if $D_A = D_B$. If $D_A \neq D_B$, there is a net flux of faster diffusing element away from regions near the sink, resulting in “depletion” of that component near the sink. Same process will also take place in the case of interstitials, with the only difference that the atom fluxes and the defect fluxes are in the same direction. The two mechanisms, i.e. interstitial flux & vacancy flux, will be operating simultaneously and the depletion or enrichment observed near the sink will be a net result of the two.

INFLUENCE OF POINT DEFECTS IN MICROSTRUCTURE OF THE LATTICE:

Irradiation results in formation of new phases or dissolution of existing phases or alters the kinetics of pre-existing phases. These processes happen either by (1) direct impingement effect i.e., the ballistic effects or (2) change in micro-chemistry via the radiation enhanced segregation or sometime, (3) alters the relative stability of phases present in an alloy. The dissolution of highly stable fine dispersoids of ytria particles in oxide dispersed steels is the example of the first type. The size distribution optimized for specific properties is changed because of recoil dissolution during irradiation. The nickel in stainless steel gets enriched near dislocations that a new phase called the G phase forms under irradiation, which is not predicted by phase diagrams. However, if an alloy is made corresponding to the chemistry of the area in which radiation enhanced segregation has taken place and thermally aged, the G phase is found to occur. The irradiation induced point defects, react with solute elements in Ni-Si alloy and Ni_3Si precipitates are found to precipitate at conditions not predicted by the phase diagram. The enhanced vacancy concentration many times accelerates the kinetics of precipitation. The third mechanism is observed in many instances. For instance, the irradiation induced point defects, can completely destroy the crystallinity of a crystal and transform it to a completely amorphous material. This is due to the increase in the free energy of the crystal with defects that at some concentration of defects, the free energy of the amorphous material is less than crystalline state.

While macroscopic behaviour of a material under irradiation is being studied, the possibilities of all the above processes need to be taken into account.

The response of a lattice with different defect configurations, when subjected to external engineering stresses, is vastly different from the normal material. The five damage mechanisms, of immediate consequence to the engineering design of the material are as follows: void growth, irradiation growth, irradiation hardening, irradiation creep and irradiation embrittlement. These are mainly caused by the point defects, linear, planar and volume defects introduced during irradiation. Each of the damage mechanism will be dealt in detail, in the second chapter.