Grain boundary segregation of impurity elements in reactor pressure vessel steels

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Grain Boundary Segregation of
Impurity Elements in Reactor
Pressure Vessel Steels.

by
Duncan Meade, BEng.(Hons.), MSc.

Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of
Philosophy of Loughborough University, December 1998

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Abstract

The segregation of a number of impurity elements to grain boundaries in reactor pressure vessel steels, under both thermal and irradiation conditions, have been observed to cause embrittlement. In low alloy steels, the embrittlement has been associated with small additions of phosphorus to alloys, an impurity element that lowers the cohesive strength of grain boundaries, thereby permitting brittle, intergranular fracture to occur more easily. Conversely, carbon additions to the same steel alloys have been shown to increase the grain boundary cohesiveness, thereby reducing the propensity for the alloy to fail in an intergranular manner. An increased understanding of the behaviour of these alloys under typical reactor service conditions is therefore sought after.

Experimental grain boundary segregation data is available for long-term thermally aged material, and theoretical models exist which can reasonably predict the magnitude and temperature dependence of impurity element segregation. Isothermal ageing-induced segregation, known as equilibrium segregation, has been predicted using a variety of analytical models, that can predict the effect of alloying elements that both interact during segregation and that segregate competitively.

However, grain boundary segregation data for irradiated material is scarcer, primarily owing to the difficulty of dealing with radioactive samples, but also due to the relative scarcity of material itself. Theoretical models, based on thermal non-equilibrium types of segregation, currently exist but are somewhat limited in their approach, since they only predict segregation in binary alloys. These models have been extended in this Thesis to predict the behaviour of ternary alloy systems. Comparison with currently available experimental results has shown that these modifications have resulted in a more accurate prediction of the segregation behaviour of these impurity elements.

In addition, the effect of thermally induced segregation has been incorporated into theoretical models to predict the behaviour of $\text{M}_{23}\text{C}_6$ type precipitates under long term thermal ageing conditions in austenitic stainless steels. These predictions have also been compared to experimentally observed precipitation behaviour in a number of alloys and have been found to show close agreement.
Acknowledgements

This work has been completed with considerable help and support from a number of people. In no particular order, I would therefore like to extend sincere thanks to the following people...

My parents, Barry and Barbara, and my sisters, Rebecca and Katherine, and my relatives, for an unmeasurable amount of support, especially when things got sticky. You don’t know how much I owe you...

Prof. Roy Faulkner (IPTME, Loughborough University), firstly for considering me for the project, and subsequently for continued support and guidance throughout the project.

Dr. David Ellis (Rolls Royce & Associates Ltd, Derby), for instigating the project of work, and subsequently keeping the project on track.

The technicians at the IPTME, for their valuable knowledge and advice.

To the Towers lads (Peds, Jonboy, Dave, Geordie, Delboy, Dammers, and co.)... Morning! (Need I say any more?)

Colin, Dave, Matt, Luke and the rest of the IPTME research students, for keeping me on my toes.

The lads (and lasses) who I’ve met through cycling. Especially to Nug and Haggie for reminding me of my roots... see you both on the Valley ride!

The John Phillips crowd (Ruth, Emma, Tim, Mark, Gunny, Shaun...)

The gang from Rainham Mark Grammar School...

And last, but not least, Scouse, for introducing a gullible fresher to University life!
Nomenclature

\( \beta \)  Constant related to grain boundary vibrational entropy.
\( \delta \)  Numerical factor.
\( \gamma_{gb} \)  Grain boundary energy.
\( \tau \)  Incubation time of precipitate.
\( \psi \)  Angle between grain boundary and precipitate.
\( \theta \)  Quench rate.
\( \rho \)  Temperature dependent dislocation density.
\( \rho_a \)  Molar density of matrix.
\( \rho_p \)  Molar density of precipitate.
\( \sigma_{aa} \)  Interfacial energy of \( \alpha: \alpha \) interface.
\( \sigma_{ab} \)  Interfacial energy of \( \alpha: \theta \) interface.
\( a \)  Lattice parameter.
\( A_v \)  Vibrational entropy of atoms around interstitial.
\( A_v \)  Vibrational entropy of atoms around vacancy.
\( A_C \)  Collector plate area.
\( b \)  Interstitial jump distance.
\( B \)  Dose rate correction factor.
\( C_b \)  Grain boundary concentration.
\( C_{b(t)} \)  Grain boundary concentration at time \( t \).
\( C_C \)  Carbon concentration.
\( C_g \)  Bulk concentration.
\( C_i \)  Impurity concentration.
\( C_v \)  Vacancy concentration.
\( C_v^0 \)  Thermal equilibrium vacancy concentration.
\( C_v^I \)  Irradiation created vacancy concentration.
\( C_x \)  Concentration at distance \( x \) from grain boundary.
\( C_{x(b)} \)  Grain boundary concentration during desegregation.
\( d \)  Grain boundary width.
\( D_{aa} \)  Diffusion coefficient of solute along interface.
\( D_{gfa} \)  Complex diffusion coefficient at the ageing temperature.
\( D_{CTS} \)  Complex diffusion coefficient at temperature \( T_s \).
\( D_i \)  Impurity element diffusion coefficient.
\( D_{SC} \)  Pre-exponential constant for diffusion of complexes.
\( D_{SI} \)  Pre-exponential constant for diffusion of interstitials.
\( D_{JS} \)  Pre-exponential constant for diffusion of solute.
$D_{0V}$  Pre-exponential constant for diffusion of vacancies.
$D_V$  Vacancy diffusion coefficient.
$E_A$  Average activation energy for complex and solute diffusion.
$E_{0V}$  Vacancy-solute atom complex binding energy.
$E_{0I}$  Interstitial-impurity binding energy.
$E_d$  Activation energy for dislocation recovery.
$E_I$  Impurity atom formation energy.
$E_{II}$  Di-impurity atom formation energy.
$E_{II^*}$  Interstitial-impurity complex formation energy.
$E_I^*$  Interstitial formation energy.
$E_V^*$  Vacancy formation energy.
$E_{VI}^*$  Vacancy impurity complex formation energy.
$E_i$  Activation energy of the impurity element, I.
$E_{mc}$  Migration energy of complexes.
$E_{mv}$  Vacancy migration energy.
$E_s$  Interfacial surface energy of impurity atom.
$E_{sv}$  Internal surface energy of vacancy.
$G$  Dose rate.
$\Delta G_i$  Segregation free energy of non-metallic impurity element.
$G$  Shear modulus of matrix material.
$\Delta H_i^0$  Standard molar enthalpy of segregation in a dilute binary alloy.
$k$  Boltzmann's constant.
$k_c$  Constant related to complex.
$k_{0V}$  Vacancy sink strength.
$k_{0I}$  Interstitial sink strength.
$k_v$  Constant related to vacancy.
$N$  Number of atom sites at grain boundary.
$N_A$  Avagadro's number.
$Q$  Solute atom binding energy.
$r_i$  Atomic radius of the impurity atom.
$r_{I}$  bcc interstitial hole radius.
$r_v$  Internal radius of vacancy after lattice distortion.
$r_0$  Initial vacancy radius before lattice distortion.
$R$  Gas constant.
$\Delta S_i^0$  Standard molar entropy of segregation in a dilute binary alloy.
\( S \)  
Surface energy per unit area of the vacancy.

\( S_i \)  
Impurity/matrix interfacial energy.

\( t_a \)  
Ageing time.

\( t_c \)  
Critical time for desegregation.

\( t_{ef} \)  
Effective quench time.

\( t_i \)  
Time interval for calculating effective time.

\( T_a \)  
Absolute ageing temperature.

\( T_i \)  
Temperature at \( i \)th time interval

\( T_m \)  
Absolute melting temperature of material.

\( T_{0,STm} \)  
Absolute temperature at which diffusion of complexes is assumed to cease.

\( T_s \)  
Absolute starting temperature of quench.

\( T_0 \)  
Absolute finishing temperature of quench.

\( v \)  
Vibrational frequency of solute atom.

\( V_a \)  
Atomic volume of solute.

\( V_0 \)  
Molar volume of precipitate phase.

\( w_{sci} \)  
Width of solute concentrated layer.

\( x_a \)  
Solute concentration in matrix.

\( x_b \)  
Solute concentration in precipitate phase.

\( x_o \)  
Mole fraction of solute in matrix.

\( x_b \)  
Grain boundary solute concentration.

\( x_{a}^{\partial} \)  
Concentration of solute in matrix at interface.

\( x_{i}^{\partial} \)  
Concentration of I at equilibrium (infinite time) at the grain boundary, \( \phi \).

\( x_i \)  
Concentration of I dissolved in the matrix.

\( x_{a}^{\partial} \)  
Total ratio of all the sites available at the interface for segregation.

\( \gamma_{i}^{\partial} \)  
Concentrations of I and M in their sub-lattices at the boundary.

\( Z_i \)  
Interstitial bias factor.

\( Z_v \)  
Vacancy bias factor.
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## Chapter 10: Conclusions and further work

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Appendix A: Program listings
Chapter 1: Introduction

The environment within a nuclear reactor is one of the most hazardous to which an engineering material could be subjected. Within a typical electrical power-generating reactor, the environment is such that the materials used for structural components must withstand severe thermal and irradiation effects, as well as corrosive attack. The behaviour of materials subjected to simple thermal treatments has, however, been well documented. Take, for example, the heat treatment of aluminium alloys to produce very strong, light materials that typically find applications in the aerospace industries. Likewise, the science of corrosion prevention is also advanced, and much work has been performed on common engineering materials to improve their behaviour in corrosive environments. A good example is the corrosion resistance of stainless steels. These particular materials are well suited to applications in chemical engineering, where both high strength and corrosion resistance are pre-requisites. However, the science of microstructural irradiation-induced damage in materials is relatively new, and has only been under development since the first nuclear reactors were designed. Likewise, predicting long term microstructural behaviour of technological alloys is also under continual modification and development.

The application of nuclear reactions to supply electrical energy to meet society's demands has been with us since the Second World War. In this time, the design of the reactors has improved, due to both advances in nuclear physics and advances in the science of metallurgy. This latter field has expanded to consider the theoretical effects of irradiation on many materials, as well as investigating the various phenomena by using a number of experimental techniques. With this improved knowledge, engineering materials have been developed to exhibit well-defined properties under typical reactor conditions. In addition, theories have been developed to predict the behaviour of these materials during service life.

The work in this Thesis covers the development of theoretical models to predict the microstructural behaviour of materials that are commonly used in the construction of nuclear reactor pressure vessels. The materials used vary between reactor system. Typically, however, the materials used are either low alloy steels or stainless steels. These materials have both been the basis of a considerable amount of research aimed at characterising the various thermally and irradiation induced phenomena that may occur during service conditions, and much of this work will be discussed throughout this Thesis.

It is known, for example, that phosphorus additions to many grades of low-alloy steel can cause weakening of the grain boundaries, leading to embrittlement during isothermal ageing or during prolonged constant temperature service conditions. This manifests itself by causing dramatic brittle fracture of components along these weakened grain boundaries. This is in contrast to ductile failure, which occurs through permanent plastic deformation of the component prior to failure.
In addition, it has been shown that additions of carbon to some low-alloy steels can suppress the degree of phosphorus-induced embrittlement, by causing the grain boundary regions to bind together more strongly. Other alloying elements that influence the microstructural evolution of materials are manganese and molybdenum, which have been found to alter the behaviour of the phosphorus within the alloy. Copper has also been found to be critical to the microstructural behaviour of irradiated low-alloy steels that are used in the construction of reactor pressure vessels, since it has been observed to form very fine grain boundary precipitates.

The aim of this Thesis is to develop a range of computer modelling techniques to forecast more accurately the microstructural changes that occur in materials used for the construction of nuclear reactor pressure vessels. The variables that influence these changes are the reactor temperature, the reactor irradiation conditions, as well as any prior-to-service heat treatments to which the material may have been subjected. In order to cover all of these subject areas, the Thesis has been written in the following way.

**Chapter 2** introduces the various effects of radiation on typical engineering materials. The physical laws of nuclear reactions will be briefly discussed, since these in turn influence the operation of the various reactor designs. Descriptions of the various designs of nuclear reactors will be made, which will highlight the structural materials used in each of the different designs. The Chapter will then introduce thermal and irradiation-induced metallurgical phenomena, some of which that will be discussed in detail in subsequent Chapters. Although not all of the phenomena that occur will be theoretically modelled, it is hoped that this section will give a feel of the complexity of the problem.

**Chapter 3** discusses the various experimental techniques that are available to materials scientists and engineers to examine materials. These techniques are used to gather data that can indicate how materials are responding to the thermal and radiation conditions that exist in the nuclear reactor. Some of the techniques discussed have been used within the scope of this work to obtain experimental results which will be used to validate the predictions obtained from the computer modelling techniques developed.

**Chapter 4** could be best described as a results section. Results obtained from the use of a range of analytical techniques described in Chapter 3 will be presented. These results were obtained from simulated post-weld heat-treated samples, as well as results of analyses performed on irradiated material. The results will form the basis for the comparison and validation of the models that will be employed in order to predict the microstructural behaviour of the materials.

Following the results section of the Thesis, a detailed description of the various techniques for modelling microstructural evolution in materials will be presented. The first of these modelling Chapters (Chapter 5) will describe the approach adopted to model the thermally induced phenomenon of segregation. The Chapter begins with a review of the
literature, so that the model developed can be examined in context to other work that has been performed. This layout of introducing previous literature prior to the modelling details is employed in all of the modelling Chapters presented. Computer listings of the programs used in this Chapter, together with those in later Chapters, are all to be found in Appendix A. The programming language used was Microsoft Visual Basic, and therefore only the relevant subroutines are listed.

Perhaps the most important chapter follows on from the thermally-induced segregation chapter. The phenomenon of radiation-induced segregation is introduced in Chapter 6. Again, a literature review of pertinent work is presented, prior to detailed descriptions of the computer models that have been applied to the material being investigated. Predictions from the models will be presented, and the results will be compared with the observed behaviour of the material that has been described in Chapter 4.

One of the most interesting aspects of the modelling work is presented in Chapter 7. This chapter describes the modelling approach that has been employed to predict the precipitation behaviour of a commonly used structural engineering material. This Chapter essentially stands on its own as a piece of work, since the material being modelled is different to that material that has been modelled in the preceding chapters. However, the modelling approach that has been adopted is worthy of detailed description, since it is tailored to the prediction of microstructural behaviour in material that has seen service for tens of years.

An altogether different modelling approach is described in Chapter 8. The work here is a model that considers the behaviour of materials on an atomic level. Again, the work is somewhat of a sidetrack to the main areas of interest. However, the approach to modelling used can be used as a comparison to the other models presented in this work.

The final Chapters of this Thesis are the discussion and conclusions. The discussion will attempt to bring together all of the work that has been performed. The limitations of each modelling technique will be analysed, as will the limitations of the experimental work that has been performed. It is hoped that the reader will, by this stage, have reached similar conclusions as those presented.
Chapter 2: Background to the effects of radiation on materials

2.1 Introduction

In order to make detailed discussion in subsequent chapters about the nature of thermal- and radiation-induced microstructural damage in reactor pressure vessel (RPV) steels, an insight into the field of nuclear power generation would be useful. In this Chapter, the concept of how energy is supplied by nuclear reactions will be introduced, together with how these reactions are controlled. This Chapter will also briefly highlight the various nuclear reactor designs and the range of materials used in their construction, as well as introducing some of the deleterious thermal and radiation effects on materials.

2.2 Nuclear reactor design

There are several designs of nuclear reactor currently in service, together with several designs for future reactors that are under development. These various reactors can be divided into two groups, fission reactors and fusion reactors. In a fission reactor, atoms of high atomic number\(^1\), such as Uranium (U) and Plutonium (Pu), are split into smaller elements, causing the release of energy. This energy, in the form of heat, can be used to generate steam that powers turbines, which in turn create electricity. Fusion reactors, on the other hand, 'fuse' light atoms, such as hydrogen. This process results in the release of energy, which can be converted into electrical energy. Recent advances in fusion technology have attained break even, where the energy going in to the system to fuse the atoms is matched by the energy given off from the reaction.

The technology surrounding the design of fission reactors has now been with us for many years. Indeed, the first controlled nuclear reaction was performed on December 2, 1942 by Dr. Enrico Fermi, using the demonstration reactor known as Chicago Pile 1. During the Second World War, there was a considerable amount of research performed in the area of nuclear technology, but the majority of research pertained to the use of uncontrollable nuclear reactions as a weapon. This type of reaction has been most graphically illustrated in the atomic bomb explosion at Hiroshima, Japan during the Second World War.

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\(^1\) The atomic number of an element is the number of protons in the nucleus of an atom. This figure is also equal to the number of electrons that revolve around the nucleus. This figure thus determines the chemical properties of an element as well as its position in the periodic table. Isotopes of the same element will all have the same atomic number, although the mass number (total number of protons and neutrons) will differ.
It was not until December 20, 1951 that the first electrical power was obtained from an experimental reactor. This reactor provided sufficient electricity to illuminate 4 light bulbs. Following on from these early milestones, the first nuclear submarine, the USS Nautilus, started its nuclear power reactor in March 1953. It wasn't until 1955 that the first large-scale nuclear reactor came into operation. This reactor, known as BORAX III, as it was an experimental boiling water reactor, provided sufficient electricity to power the town of Arco, Idaho, with a total population of 1000. The Calder Hall reactor, a gas cooled reactor, went into operation in the UK in 1956, producing both electricity and plutonium. In December 1957, the first full-scale nuclear power plant went into service at Shippingport, Pennsylvania. This reactor operated until 1966 and was able to generate 60 megawatts (MW) of electricity.

In 1963, plans for the first nuclear reactor that could supply sufficient energy to be competitive with more common fossil fuel plants were drawn up. In 1965, the first small-scale nuclear reactor operated in space. This reactor weighed a meagre 435kg and supplied 580 watts of electrical power. Around this time, there were also plans for nuclear powered aircraft, as well as nuclear powered space rockets. Further details surrounding these projects can be found in "Nuclear Energy" by Raymond Murray[1].

By the 1970's, the pace of development had rapidly accelerated. There was a significant amount of research aimed at developing a class of reactor termed breeder reactors (discussed later). In 1973, there were orders for 41 nuclear power plants within the U.S. alone. In 1974, the first 1 gigawatt (GW) nuclear plant became operational, the Commonwealth Edison Zion 1. However, in March 1979, the first major nuclear incident took place. It occurred at the Three Mile Island plant in Harrisburg, Pennsylvania. This accident bought the publics attention to the negative aspects of using nuclear energy. Luckily, no one sustained any direct injuries because of the accident.

In 1980, nuclear energy generated more electricity than oil fuelled power stations. By 1983, nuclear energy had also overtaken natural gas, and in 1984, it overtook hydropower to become the second largest source of electricity. At this time, the largest source of electricity remained coal. The 100th U.S. nuclear power plant was built in 1986, known as the Perry power plant, in Ohio.

In the early 1990's, nuclear power was providing around 20 percent of the electricity demand of the U.S., approximately 610 billion kilowatt-hours (kWh) of electricity. Plans were also laid to begin development of advanced, standardised power plants. The advantages that these plants hold over the previous generation of reactors will be discussed in due course. The first of these reactors to operate was the Kashiwazaki-Kariwa Advanced Boiling Water Reactor, built in Japan. This reactor began operation in late 1996.

By the end of 1997, there were 437 nuclear reactor units worldwide, with an energy production capacity of over 343GW of electricity. In the US alone, there were 105 reactors in operation[2]. This capacity accounts for around 17% of the total electricity produced[3].
Incidentally, the provision of 17% of the world's annual electricity consumption by nuclear power has prevented the emission of 2.3 billion tonnes of carbon dioxide each year\[4\]. It is for this reason that nuclear power is seen as having a major role in the reduction of greenhouse gas emissions.

Fusion reactors, on the other hand, are still being developed, and optimistic estimates suggest that the first fusion reactor will not operate for at least 30 years. However, as the reader will gather later, the technology of fusion reactors will effectively make fission reactors redundant owing to the highly abundant fuel source.

The following discussion will be divided into the two nuclear reactions mentioned. The physics behind the reactions will be briefly described, as this will be of use when discussing radiation damage processes later in the chapter. Additionally, the various current designs of fission reactors will be discussed in some detail. The proposed design of future fusion reactors will only be briefly discussed.

2.2.1 Fission reactors

As mentioned earlier, the principle of operation of a fission reactor lies in the splitting of atoms of high atomic number into smaller particles, having the consequence of releasing energy. Typically, the elements used in the process are isotopes of uranium and plutonium, depending upon the class of fission reactor. Uranium occurs naturally, with the most common isotope being the fertile isotope \(^{235}_{92}\text{U}\) with around 0.711 wt.% being the fissile isotope \(^{239}_{92}\text{Pu}\). Fissile isotopes are those used as fuel for the majority of reactor designs, are those isotopes that can undergo fission during bombardment of neutrons with low energy. These neutrons are termed 'slow' or 'thermal' neutrons. Fertile isotopes, alternatively, can undergo fission to create fissile isotopes. This property of certain isotopes is utilised in the design of breeder reactors, to be discussed later in this chapter. Plutonium (\(^{239}_{94}\text{Pu}\)) is a man-made fissile isotope, as is \(^{235}_{92}\text{U}\). These two artificial isotopes are created from neutron irradiation of the fertile elements of \(^{238}_{92}\text{U}\) and \(^{232}_{90}\text{Th}\).

Since the percentage of fissile material that occurs naturally is so low, it is necessary to enrich the fuel somewhat to make it into a more suitable form. It is therefore necessary to separate the various types of uranium that are found naturally. The process of isotope separation is therefore critical to reactor operation. There are various methods to separate isotopes. These processes can be classed as (1) mass spectrograph, (2) gaseous diffusion, (3) gas centrifuge, and (4) laser isotope separation. Descriptions of these techniques can be found in the literature\[3\].

When we consider the energy release from fission reactors, the chain reaction that occurs is controlled using a moderator. A typical fission reaction can be explained by the following process.
$^{235}\text{U}$ absorbs a neutron: $^{235}\text{U} + ^1\text{n} \rightarrow \left( ^{236}\text{U} \right)^+ $ where $\left( ^{236}\text{U} \right)^+$ represents $^{236}\text{U}$ in an excited state. Since $^{235}\text{U}$ is unstable, a typical fission process would result in the atom fragmenting into several smaller nuclei. A typical fission process would be $\left( ^{236}\text{U} \right)^+ \rightarrow ^{90}\text{Kr} + ^{136}\text{Ba} + ^2\text{n} + E$ resulting in fission fragments of krypton and barium, together with a release of 2 neutrons as well as an amount of energy. The amount of energy is proportional to the difference in the atomic weights of the fission fragments and the uranium fuel.

The energy released from such a process would be approximately 200 MeV$^2$, depending upon the exact fission fragments produced. The complete fission of 1 gram of uranium produces approximately 1MW-day of electricity, which is the same as the energy released through the burning of 2.5 tons of coal$^5$. This statistic itself demonstrates the advantage of nuclear energy. Transportation of fuel is minimised, since there is little fuel used, compared to the burning of fossil fuels. Environmentally, the release of greenhouse gases, an area of great concern currently, is minimised by using nuclear energy. It has also been calculated that for a 3000MW nuclear reactor, the consumption of $^{235}\text{U}$ is of the order of 4kg per day$^1$.

Since more neutrons are given off than are required to initiate the process, the fission process requires a means of absorbing these excess neutrons in order to prevent a chain reaction. Thus, the moderator type is of importance to reactor design.

Having classed nuclear energy into two processes, it is now possible to sub-categorise the design of fission reactors. The main differences between the various fission reactors lies in the speed of the neutrons that are released from any given reaction. These neutrons can be classed as either thermal neutrons, or fast neutrons. Fission reactors can thus be categorised as either thermal reactors or fast reactors. The discussion will now highlight the various differences between these two classes.

Further discussion on the design and development of fission reactors, beyond that given here, can be found in many sources, in particular the web-site of the International Atomic Energy Authority$^6$, and "A guidebook to nuclear reactors" by Nero$^7$.

### 2.2.1.1 Thermal reactors

Thermal reactors are classes of reactor where a moderator is used to slow the neutrons given off in the nuclear reaction. The neutrons need to be slowed to such a speed and energy that they are more likely to cause fission in further atoms. In a typical reaction, there are 2.5 neutrons released during each fission process. The total energy of these

---

$^2$ The work done on an electron that it is displaced through a potential difference of 1 volt. $1\text{eV} = 1.60218925 \times 10^{-19}\text{joule}$. 

7
neutrons is around $10\text{MeV}$, giving a mean energy of around $4\text{MeV}$ per neutron. Note, however, that this figure is a mean of all the energies of the neutrons. There will therefore be neutrons with a wide range of energies. If a moderator is used to slow these neutrons, there is a higher probability that they will cause fission as opposed to purely being captured by uranium atoms.

The selection of a suitable moderator for a reactor system depends on the characteristic 'age' of the neutron moderator. Since neutron moderation is a statistically random process, a number of steps will be passed through for the neutron to slow down from being classed a fast neutron to a thermal neutron. Thus, the distance through which a neutron must pass to become a thermal neutron is the definition of neutron age. Table 2.1 shows the calculated neutron ages for various moderators.

<table>
<thead>
<tr>
<th>Moderator</th>
<th>Age to thermal, $\tau$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light water (H$_2$O)</td>
<td>26</td>
</tr>
<tr>
<td>Heavy water (D$_2$O)</td>
<td>125</td>
</tr>
<tr>
<td>Graphite (C)</td>
<td>364</td>
</tr>
</tbody>
</table>

Table 2.1: Moderator efficiencies (from Murray$^{[1]}$)

It can be seen from the table that light water is the most effective moderator, since it slows neutrons to thermal levels far more rapidly than both heavy water and graphite. Light water is used as a moderator in the designs of certain pressurised water reactor and boiling water designs. These will be discussed in due course.

In addition to moderators, fission reactors also employ a coolant system. The coolant system is used to remove heat from the reactor and enable it to be passed through a system containing steam generators. These generators are within a system containing suitable turbines, which create the electrical energy. For example, the design of the High Temperature Gas-cooled Reactor utilises a system of three turbines, which operate from the high, intermediate and low pressure coolant systems. The choice of coolant for a reactor system depends upon the reactor system. For example, some systems employ a single moderator/coolant system, whereby one medium is used as both moderator and coolant. Many reactor designs employ separate moderator and coolant systems.

<table>
<thead>
<tr>
<th>Inlet temperature</th>
<th>250-400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. temperature</td>
<td>650-700°C</td>
</tr>
<tr>
<td>Most non-fuelled components</td>
<td>400-560°C</td>
</tr>
</tbody>
</table>

Table 2.2: Typical temperatures found within reactor components

The materials requirements for nuclear reactors vary, depending upon the position within the reactor, together with the proximity of radiation. The data presented in Table 2.2 gives an indication of the types of environments that can be expected. The materials used
must therefore be compatible with the coolant and moderator medium, as well as retain mechanical strength at the temperature at which the component is operating.

**Boiling water reactors**

This design of nuclear reactor is probably the simplest of them all. The light water is contained in a single circuit, and acts as both moderator and coolant within the reactor. Typically, the pressure of the water is around 7MPa and the temperature is in the region of 280°C. The reactor pressure vessel is typically constructed of steel, surrounded by a shield of concrete. The schematic of a boiling water reactor is shown in Figure 2.1, showing the circulation of the coolant/moderator water through the reactor core.

![Figure 2.1: Boiling water reactor schematic (bwr1.tif)](bwr1.tif)

The fuel used in BWR systems is usually slightly enriched Uranium, containing between 1 and 3 percent $^{235}$U. The fuel rods are contained within tubes constructed of Zircaloy\(^1\). In order to prevent the power peaking in the centre of the reactor core, the fuel rods are enriched in proportion to the distance from the centre of the core. This technique is commonly referred to as the cyclic, three-zone loading system. A large BWR reactor core could contain up to 50 000 fuel rods, and weigh in the region of 160tons.

The first example of the BWR design was the Dresden nuclear power plant, which started operation in 1960 with an electrical power output of 200MW. The latest development of these reactor designs are known as Advanced Boiling Water Reactors, abbreviated to ABWR. The specifications are for a power output in the range of 1300MW.

**Pressurised water reactor**

In comparison to the boiling water reactor design just discussed, the pressurised water reactor has separate circuits for the coolant and moderator of the reactor, and for the

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\(^1\) Zircaloy is an alloy containing around 98% zirconium, with additions of tin, iron, nickel and chromium. It has low neutron absorption, and is sufficiently resistant to chemical attack together with thermal and irradiation damage from thermal reactors.
steam generating circuits. This is shown diagrammatically in Figure 2.2. The pump in the primary coolant circuit maintains a water pressure of 15.5MPa within the reactor core. In comparison to the BWR system, the coolant is at a slightly higher temperature, typically 325°C. Immediately adjacent to the fuel cladding, however, the coolant can reach temperatures of up to 370°C. As with the BWR, the reactor pressure vessel is a steel structure, enclosed within an outer concrete shield.

![Figure 2.2: Pressurised water reactor schematic (pwr1.tif)](image)

The reactor core comprises of around 180 fuel elements, with 20 or so positions available for the insertion of the silver-indium-cadmium control rods. Each of the fuel elements contains 200 fuel pins, and is roughly 20cm square. The fuel pins themselves are roughly 4 metres long, and are thin shelled Zircaloy-4 tubes with a wall thickness of 0.6mm. The Zircaloy-4 used for PWR fuel rods is a slightly different specification to that used in BWR fuel rods, which is typically Zircaloy-2. These fuel pins contain the fuel pellets and prevent them from interacting with the coolant medium, as well as containing the fission products that are produced during the nuclear reaction. The fuel pellets are slightly enriched $^{235}{\text{U}}$ to between 2.5 and 4 percent in the form of uranium dioxide ($\text{UO}_2$). Each pellet is 1cm in diameter and 1.5cm in length. In total, the weight of a typical PWR core is 100tons.

As with the core of the BWR system, the PWR design incorporates a feature to prevent the centre of the reactor from having a higher power density. In the PWR design, the core is made from an annular 'seed' of enriched fuel, which is clad internally and externally with blankets of natural Uranium. This process is termed the seed blanket loading system. This system of loading means that the average power density of PWR cores is around 98kW per litre. This energy is removed from the core using the pressurised water coolant, which flows at a rate of 18000 litres per second.

The next generation of PWR systems could be the Light Water Breeder Reactor (LWBR). These reactors would employ the thorium-uranium fuel cycle, which is more efficient than the low-enrichment uranium-plutonium cycle currently used.
Heavy water reactors

The designs of the BWR and PWR systems both utilise light water as both coolant and moderator. Recalling Table 2.1, light water has the lowest neutron age, and thus is the most efficient moderator for slowing high-energy neutrons to thermal energies. The best example of a Heavy Water Reactor (HWR) is the CANDU (Canadian Deuterium Uranium) design. This design is significantly different to both BWR and PWR systems. In the light water reactor systems described, the core is held in a vertical orientation, and all the fuel rods that make up the core are held within one pressure vessel. This approach therefore requires the reactor to be shut down for the core to be reloaded.

The CANDU design uses individual pressure tubes to hold the fuel rods. These pressure tubes are held within a calandria in a horizontal orientation. These features allow the reactor to be refuelled whilst the reactor is operational. A 600MW reactor would typically contain around 4500 bundles of fuel pins, with around 15 bundles replaced per day.

These pressure tubes contain heavy water as a moderator, and the whole structure is cooled with heavy water. The moderator contained within the pressure tubes is maintained at approximately 10Mpa, and the coolant exits the reactor at a temperature of 310°C. The coolant flow rate for this reactor system is 7600 litres per second. However, the thermal efficiency of these reactors is lower than the light water reactors previously discussed, at between 28 and 30 percent compared to between 32 and 34 percent.

Gas-Cooled Reactors

There are two basic designs of gas-cooled, graphite moderated, reactors. These are the Advanced Gas-cooled Reactor (AGR) and the High Temperature Gas-cooled Reactor (HTGR). The AGR design has been used with some success in the UK, since the Calder Hall reactor that went into operation in 1956. These reactors have become termed 'Magnox' reactors, owing to the use of magnesium oxide as the fuel-rod cladding material.

The designs of both AGR and HTGR essentially follow the design of the pressurised water reactor, having a primary coolant system which in turn feeds a secondary steam generating system to power the turbines. In the PWR system, the primary coolant system used pressurised water. The design of AGR systems utilises carbon dioxide (CO₂) as the coolant, whereas the HTGR design utilises helium gas. The moderator used in both systems is graphite. The graphite, in the form of rods, can be inserted into the reactor in place of standard fuel rods. In case of a reactor meltdown, where the reactor is out of control, these rods can drop into place due to gravity, and bring the reactor back under control.

In the design of the Calder Hall GCR, the maximum operating temperature of the CO₂ coolant was only 345°C, owing to the chemical reaction between the CO₂ coolant and the graphite moderators. This had the consequence of lowering the overall operating efficiency of the reactor, and causing the power generating capacity of the reactor to be quite low. The
improved designs of the AGR and HTGR increase the operating efficiency of the reactors together with increasing the power output available.

The AGR design uses fuel rods containing \( \text{UO}_2 \) of slightly enriched \( ^{235}\frac{\text{U}}{\text{U}} \), roughly 1.2 to 1.5 percent. As mentioned, the fuel cladding is magnesium oxide. Magnesium is particularly good as a fuel cladding material, since it is compatible with both the \( \text{UO}_2 \) fuel and the \( \text{CO}_2 \) coolant. It is also resistant to corrosion from \( \text{CO}_2 \) up to around \( 400^\circ \text{C} \), and its mechanical strength and ductility do not significantly change under neutron irradiation. However, its corrosion resistance to water and sodium are poor. For this reason, it cannot be used in alternative reactor designs, such as the PWR and BWR designs discussed, and the LMFBR design discussed in the following section.

In contrast, in the HTGR design, the fuel is highly enriched (approximately 14%) \( ^{235}\frac{\text{U}}{\text{U}} \) with 85% thorium and 1% \( ^{238}\frac{\text{U}}{\text{U}} \). Some designs, however, require an initial fuel load to contain up to 93% \( ^{235}\frac{\text{U}}{\text{U}} \). The particulate fuel is held in dense, impervious pyrolytic graphite blocks, which are stacked to form the reactor core. The helium coolant in the reactor is maintained at high temperatures, typically \( 740^\circ \text{C} \), at pressures of around 5MPa and flow rates of 1300 kg per second. This high core temperature is attainable since there is no metal cladding that could be sensitive to high temperature operation. The whole of this reactor and its steam generation systems are also contained within one concrete vessel. Of the thermal reactors described thus far, this design has the highest thermal efficiency of approximately 39%.

2.2.1.2 Fast (breeder) reactors

The design of a fast breeder reactor has no moderator to slow the free neutrons, hence the terminology 'fast'. The energies of these fast neutrons, therefore, are typically in the range of 2MeV. Owing to this high neutron energy, it is possible to 'breed' fissile fuel from fertile fuel materials. In the various fertile materials, it is found that \( ^{239}\frac{\text{Pu}}{\text{Pu}} \) is the most likely fertile material to breed fissile material. Another suitable candidate for fast reactors is \( ^{235}\frac{\text{U}}{\text{U}} \). However, it has also been found that \( ^{233}\frac{\text{U}}{\text{U}} \) could be used to breed fissile material using slower thermal neutrons.

The breeding of fissile fuel is due to the theoretical reproduction factor of neutrons, \( \eta \). If \( \nu \) is the number of neutrons produced per atomic fission, and \( \sigma_f/\sigma_a \) is the fission to absorption ratio of the neutrons in the fuel, then the reproduction factor can be expressed as:

\[
\eta = \frac{\sigma_f}{\sigma_a} \nu
\]  

(2.1)

The reproduction factor has been found to increase proportionally with neutron energy, therefore making breeding of further fuel more likely. This is because there are more neutrons available both for fission of fissile fuel and conversion of fertile fuel.
The first breeder reactor to generate electricity was the Experimental Breeder Reactor I (EBR-I), at Idaho Falls in the USA in 1951. Since then, several experimental reactors have been built around the world. Of these, perhaps the most important was the Fast Flux Test Facility (FFTF), in Richland, Washington. This reactor has supplied valuable data relating to materials performance within nuclear environments[8].

The fuel used in these reactors differs significantly from those used in the moderated thermal reactors described earlier. The fuel is typically 80% $^{238}\text{U}$ with 20% $^{239}\text{Pu}$. This fuel is surrounded with a blanket of $^{238}\text{U}$, which is converted during the nuclear reactions into $^{239}\text{Pu}$. Plutonium itself can be used as a fuel for some designs of nuclear reactor. However, in the wrong hands, plutonium is the main material for the construction of nuclear warheads, and as such is more closely controlled than uranium. Liquid metal fast breeder reactor's (LMFBR's) breed $^{239}\text{Pu}$ from the non-fissile isotope $^{238}\text{U}$. It has been calculated that by the year 2000, the waste uranium from the currently operating thermal reactors would be sufficient fuel for fast reactors to supply current levels of energy for over a thousand years[5].

Another advantage of fast reactors is their compact size. Since no moderator is required, the power density of the reactor core is high, meaning that the actual size of the reactor can be small. However, fast reactors cost considerably more than thermal reactors to construct. This is primarily due to the type of coolant used to control the reactor. Thermal reactors typically use light water as both a coolant and a moderator, which can be found abundantly and therefore cheaply. Since fast reactors need no moderator, coolants that do not slow the neutrons within the core are used. Examples of the coolants used are liquid sodium and helium. Liquid sodium is an efficient coolant, but becomes radioactive during operation, producing the isotope $^{24}\text{Na}$, with a 15hour half-life. High-pressure helium gas is also used. This has the advantage over liquid sodium that it does not become radioactive and absorbs fewer neutrons.

2.2.1.3 Thermal reactor materials

A summary of the range of materials that are employed in the construction of these thermal reactors is shown in Table 2.3. This table does not include the various materials that are used as cladding materials, as the work of this thesis is based around the structural RPV materials. The table shows that for the light water reactor designs, carbon steels predominately in the construction of the pressure vessel. In the design of the liquid metal reactors, and the gas-cooled reactors, the pressure vessel material must be resistant to the coolant medium, either liquid sodium, $\text{CO}_2$ or helium.
### Reactor Types and Power Densities

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Relative power density</th>
<th>Relative vessel size</th>
<th>Vessel material</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGR, HTGR</td>
<td>Very low - low</td>
<td>Very large</td>
<td>Pre-stressed concrete, stainless steel lining</td>
</tr>
<tr>
<td>PWR</td>
<td>high</td>
<td>Thick, medium</td>
<td>Carbon (silicon) steels, A53B, A533B, A212B, stainless steel lining (type 304L SS)</td>
</tr>
<tr>
<td>BWR</td>
<td>medium</td>
<td>large</td>
<td>Carbon steels, A302B, A212B, A533B, A53B, stainless steel lining</td>
</tr>
<tr>
<td>LMFBR</td>
<td>Very high</td>
<td>small</td>
<td>Stainless steels, types 304, 304L, 308</td>
</tr>
</tbody>
</table>

Table 2.3: Materials used in the design of reactor pressure vessels (from Ma[9])

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### 2.2.2 Fusion Reactors

Currently, all energy supplied by nuclear processes uses the basic fission reaction, which has been discussed in the previous sections. This section will describe the theory behind the idea of nuclear fusion, together with information regarding the current research that is being carried out into various aspects of the fusion reaction.

It has been calculated that a fusion reaction would yield far more energy per atomic mass unit than the fission of uranium. The yield per atomic mass unit for deuterium, the probable fuel source for fusion, is approximately 6MeV, compared to the yield of 0.81MeV released by the fission of $^{235}_{92}$U[1]. An additional benefit of developing fusion is the abundance of the fuel source. Deuterium, which is a heavy isotope of hydrogen, makes up approximately 1 part in 6300 of ordinary water. There is thus a virtually inexhaustible, cheap supply of fuel. This is in contrast to other currently used fossil fuel sources, such as coal and oil, which are both becoming scarce, and to some extent uranium. Fusion energy would therefore offer an attractive alternative to all the currently used sources, and would last for considerably longer.

The theory behind the fusion reaction involves the fusing together of elements that have a very low atomic mass. An example is the fusion of 2 hydrogen nuclei and 2 neutrons. This would result in the formation of helium, with a corresponding release in energy, proportional to the weight difference of the elements before and after the reaction. The process of fusion and energy release can be shown below:

$$2^1H + 2^1n \rightarrow ^4He + 28.3\text{MeV}$$

This reaction is the main reaction that occurs within the sun, but is actually quite a slow process. For useful energy production, a more suitable fuel would be deuterium, which is a heavy isotope of hydrogen containing 2 neutrons instead of 1. Reactions that could occur during the fusion of this element are:

---

4 The atomic mass unit (a.m.u.) is a unit of mass equal to one twelfth of the mass of an atom of carbon-12. It is equal to $1.6605 \times 10^{-27}$ kg.

14
\[ ^2\text{H} + ^2\text{H} \rightarrow ^3\text{He} + ^1\text{H} + 4.03\text{MeV} \]
\[ ^3\text{H} + ^2\text{H} \rightarrow ^3\text{He} + ^1\text{n} + 3.27\text{MeV} \]
\[ ^3\text{H} + ^2\text{H} \rightarrow ^4\text{He} + ^1\text{n} + 17.6\text{MeV} \]
\[ ^3\text{H} + ^2\text{He} \rightarrow ^4\text{He} + ^1\text{H} + 18.3\text{MeV} \]
\[ ^3\text{H} + ^1\text{n} \rightarrow ^2\text{H} + 2.2\text{MeV} \]

From these reactions, it can be seen that the fusion of deuterium causes the production of tritium, another heavy hydrogen isotope with 3 neutrons present, as well as hydrogen and helium and a release of neutrons and energy. The release of energetic neutrons would in turn fuse with hydrogen to create more deuterium and additional energy. The reactions described above can be summed as:

\[ 4^2\text{H} \rightarrow 2^4\text{He} + 47.7\text{MeV} \]

However, the fusion reaction, in contrast to the fission reactions already discussed, requires the fusing particles to have very high energies. The reason for this is that as 2 nuclei approach each other, there are forces of electrostatic repulsion that exist between them, forcing them apart. Therefore, in order to overcome these forces and enable the 2 nuclei to fuse, the atoms must possess sufficiently high energy. This energy could be either kinetic or thermal. It has already been mentioned that fusion reactions occur within the sun. It can be calculated that to produce fusion, temperatures in the region of several million Kelvin are required. In order to create these temperatures on Earth, there are two possible solutions. One possible approach is the use of a fission bomb to generate a suitably high temperature so that fusion can occur. This is known as the thermonuclear bomb, or H-bomb.

The more peaceful approach to generating high temperatures is to use plasma. The plasma is highly ionised gas consisting of equal numbers of electrons and deuterium atoms so that it is electrically neutral. The plasma is held within a magnetic confinement system. This system is used to accelerate the plasma to high speeds, which in turn provide the deuterium atoms with sufficient energy to fuse. The use of such a plasma would also mean that the likelihood of a run-away chain reaction within the reactor would be minimised, since there would only be a small quantity of fuel within the reactor at any one time.

There is currently a lot of research into the various aspects of the fusion process. The Tokamak Fusion Test Reactor (TFTR) in Princeton is investigating very high plasma temperatures. The Joint European Torus (JET) at Culham is investigating the Deuterium-Tritium reaction, and the Doublet DIII-D in San Diego is investigating a method of removing debris from reactors.
There is also currently a lot of interest in fusion systems which are reaching break-even, where the amount of energy supplied to cause fusion is equal or exceeded by the energy return from the fusion reaction. Until experimental reactors are built that greatly exceed this unity value, the prospect of fusion energy will remain distant.

There are many sources of information surrounding the theory behind fusion reactors. In particular, the United States Department of Energy has a comprehensive internet site, and contains details of the research program that is currently underway. As mentioned, there are other groups around the world looking into various aspects of nuclear fusion. One group is the Australian Fusion Research Group, who are performing research into the use of a toroidal heliac-configuration particle accelerator to generate suitable plasma conditions for fusion.

Although the materials that are intended for use in the construction of these fusion reactors are not considered in the work presented in this Thesis, it is worth bearing them in mind. These materials will also be subjected to the deleterious processes imposed by irradiation, although at a considerably higher level than imposed by typical fission reactors. Additionally, the materials will be subjected to much higher temperatures, since the structural materials will need to contain the fusion plasma that will be maintained at many thousand degrees. It should be noted here that the fusion plasma is held in a magnetic field and should not, in normal use, contact the first wall structural material.

In particular, there is considerable interest surrounding the use of low activation materials as the first wall structure that contains the plasma. These materials would need to be able to withstand significant temperature fluxes, together with high mechanical loading and intense irradiation from the high-energy neutrons that are part of the fusion reaction. These materials would also help to reduce the amount of radioactive waste that would be produced by the reactor.

### 2.3 Irradiation-induced degradation of materials

So far, the discussion has been centred about the various designs of reactors, highlighting the differences in their theory and operation. No mention has been made of the problems that mechanical and materials engineers encounter when designing such reactors. It has been shown that the environment within a nuclear reactor is possibly one of the most harmful to typical engineering materials. Not only has the reactor pressure vessel got to contain the radiation, it has got to do so over a long period of time, typically in the region of 30 years or so.

In addition, fission reactor pressure vessels will be subjected to temperatures in the range of 250-400°C for the duration of the life of the reactor, and these temperatures may cause additional phenomena to take place. Table 2.4 gives examples of the criteria that are
used for selecting materials for construction of reactor pressure vessels. It can be seen that there is a range of materials that could be used. Ultimately, the selection is determined by cost and manufacturing process, since some materials cannot be easily fabricated.

<table>
<thead>
<tr>
<th>Primary requirements</th>
<th>Basic material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low neutron absorption (capture)</td>
<td>Zr, Al, Mg, Be</td>
</tr>
<tr>
<td>High mechanical strength and ductility</td>
<td>Carbon steels, stainless steels</td>
</tr>
<tr>
<td>High thermal stability (heat resistance)</td>
<td>Ni-based superalloys</td>
</tr>
<tr>
<td>Great irradiation stability</td>
<td>Refractory metals, Mo, Ti, Ta, W</td>
</tr>
<tr>
<td>Low induced radioactivity</td>
<td>Ceramics, BeO, Al₂O₃, MgO, SiO₂</td>
</tr>
<tr>
<td>Good heat transfer properties</td>
<td>ZrSi₂, SiC-Al</td>
</tr>
<tr>
<td>High temperature corrosion resistance</td>
<td>Graphite, pre-stressed concrete</td>
</tr>
</tbody>
</table>

Table 2.4: Reactor structural materials (from Mα[9])

The discussion has demonstrated what happens within a nuclear reactor, and how energy is converted from the reaction itself into a constant supply of electricity. Throughout the discussion, various features of the reactions constantly reappear. The fission reaction takes place within a reactor pressure vessel, within which coolant and/or moderator is circulated at a high temperature and through which neutrons of high-energy travel. The materials from which these pressure vessels are constructed therefore need to be able to maintain structural integrity whilst being bombarded with a range of high-energy neutrons. The material will also need to be able to resist chemical attack from the moderator or coolant. In addition to these factors, the pressure vessel will be operating at a temperature of several hundred degrees Centigrade, and will experience a range of thermal fluctuations throughout its service life.

From a metallurgical point of view, the pressure vessel will be subjected to many deleterious processes. The engineering of these components must therefore incorporate a high safety margin, since under no circumstances may any failures be tolerated. A graphic example of what may happen should a failure occur is the reactor explosion at Chernobyl. Although this type of reactor design is now outlawed, current designs of reactors must confront the possibility of reactor meltdown. Therefore, reactors must be designed such that should the worst possible scenario occur, the reactor will maintain structural integrity to prevent any radioactive leakage into the environment.

The following sections will highlight some of the varied phenomena that occur due to both thermal effects and due to neutron irradiation. The phenomena of segregation and precipitation will not be discussed here, since they will be described in considerable detail in subsequent chapters of this thesis. Where possible, reference is made to texts that contain more detail than that given here.
2.3.1 Defects within crystalline materials

The materials used in the construction of reactor pressure vessel, and indeed most other components, are crystalline in structure. This means that there is a long-range order of the structure of the material on an atomic scale. These crystalline materials can be classed according to the order that they exhibit. For example, ferritic steels have a structure termed body centred cubic; austenitic steels exhibit a face centred cubic structure; zinc and magnesium are both hexagonal close-packed structures.

<table>
<thead>
<tr>
<th>Structure-insensitive</th>
<th>Structure-sensitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic constants</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>Melting point</td>
<td>Semiconductor properties</td>
</tr>
<tr>
<td>Density</td>
<td>Yield stress</td>
</tr>
<tr>
<td>Specific heat</td>
<td>Fracture strength</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>Creep strength</td>
</tr>
</tbody>
</table>

*Table 2.5: Structure properties of materials (from Dieter[12])*

It is, however, rare for a material to be a perfect crystal structure. It will exhibit short and long-range defects. These defects may influence the large-scale behaviour of the material. *Table 2.5* shows how some material properties are structure-sensitive, and others are insensitive to any microstructural defects. From the point of view of material selection for a RPV, it can be seen that the properties of yield stress, fracture stress and creep strength are all structure-sensitive. Thus, knowledge of these variations in the microstructural layout of materials is beneficial.

2.3.1.1 Point defects

Point defects within lattice structures are those imperfections that are localised to an area of a few atoms. There are thus three categories of point defects. These can be shown schematically in *Figure 2.3 (a) and (b)*. If an atom is missing from its lattice site, the defect is termed a vacancy. Vacancies are created by thermal excitation, where an atom is given sufficient energy to jump from its regular lattice location. At any given temperature, the fraction of vacancies that are present can be determined from Equation 2.2.

\[
\frac{n}{N} = e^{-\frac{E_v}{kT}} \tag{2.2}
\]

where: n is the number of vacancies per N lattice sites  
E_v is the energy required moving an atom from its lattice position to the surface  
k is Boltzmann’s constant  
T is the absolute temperature (temperature expressed in Kelvin).
This equation, however, is only applicable to equilibrium conditions, i.e. conditions where the material is allowed to reach steady state. Should the material be suddenly quenched from a high temperature to a lower temperature, the material is not in equilibrium. In these conditions, the higher vacancy concentration that was present at the higher temperature is maintained even at the lower temperature. This situation is termed super-saturation. This effect is the cause of segregation mechanisms that involve interactions between vacancies and solute atoms, which will be covered in the discussion of Thermal Non-Equilibrium Segregation in Chapter 5. In addition to rapid quenching, it is possible to produce a higher than equilibrium concentration of vacancies by both irradiation and by mechanical working.

![Figure 2.3(a): Schematic of the vacant atomic site and an interstitial atom](image)

![Figure 2.3(b): Schematic of substitutional and interstitial impurity atoms](image)

The second category of point defect is the interstitial atom. This atom is located between lattice interstices. This type of point defect is rarely produced by thermal processes, as opposed to the vacancy discussed previously. However, it is created both by cold work, and during irradiation by energetic neutrons and will be discussed later. It is worth noting that the creation of an interstitial atom together with a vacancy is termed a Frenkel pair.

The third category of point defect is the impurity atom. This atom is not present in the material when the material is pure. However, it is rare that materials are produced entirely pure, and as such, impurity atoms will be found in many materials. In steels, for example, impurity atoms will be introduced into the material during casting processes. Recycled steel will also have a high level of impurity elements present due to the difficulties of removing low concentrations of alloyed elements.
2.3.1.2 Line defects

Dislocations, in their simplest forms, are regions of a crystal structure that contain an extra half-plane of atoms. This simple dislocation is termed an edge dislocation, and can be seen schematically in Figure 2.4 (a) and (b). The plane of atoms described by ABCD is introduced into the regular lattice structure, causing the structure to relax, and become deformed. Another form of dislocation that is can be defined is a screw dislocation, shown in Figure 2.4 (c). In this case, the lattice structure shown in Figure 2.4 (a) has been subjected to a shear force. The direction of the dislocation, termed the Burgers vector, is now perpendicular to the plane of the edge dislocation. Most dislocations are, however, a complex combination of both edge- and screw- dislocations.

![Figure 2.4: Schematic diagrams of edge- and screw- dislocations](image)

In some cases, where there are many edge dislocations close to one another, such as in Figure 2.5, the region can become a grain boundary. It can be seen that the lattice structures on either side of this boundary are different by an angle of θ. This is termed a low-angle boundary, since the angle θ is small. In the diagram, the edge dislocations are shown by the symbol L. This symbol is used in many texts describing dislocations and their behaviour in materials, such as "Introduction to dislocations" by Hull and Bacon\(^{[13]}\).

![Figure 2.5: Low angle grain boundary made from edge dislocations](image)
Dislocations are found in all crystalline materials. In engineering materials, dislocations are essential for allowing a material to plastically deform. Under loading, either steady or sudden, the dislocations within the material move, allowing the material to relieve localised strains that have built up. This movement of dislocations is termed glide, and the dislocations glide along what are known as slip planes. Should these dislocations be locked in some way, they are unable to move, and the material would exhibit brittleness. The importance of these dislocations will become apparent when discussing the effect of irradiation embrittlement.

### 2.3.2 Irradiation Induced defects

In fission reactors, the material that the reactor pressure vessel and other structural members are subjected to irradiation from energetic neutrons. In thermal reactors, these neutrons have energies in the range of 1MeV, whereas for fast reactors, these neutrons have higher energies. The previous discussion of point defects showed that neutron irradiation causes the production of interstitial atoms. These interstitial atoms are created by the energetic neutron knocking an atom from a regular lattice site into a position that lies in between regular positions. Since different energy neutrons would cause a different number of interstitial atoms to be produced, it would be helpful to determine a method of characterising the neutron damage.

Norgett and co-workers \(^{[14]}\) proposed a simple equation to equate the energy of the neutron irradiation to an irradiation damage dose and dose rate. Their definition of the number of Frenkel pairs \(^{5}\) created during irradiation, \(N_d\), is:

\[
N_d = \frac{\kappa \hat{E}}{2E_d} \tag{2.3}
\]

where:
- \(\kappa\) is the displacement efficiency
- \(E_d\) is the displacement energy
- \(\hat{E}\) is the energy available to generate atomic displacements by elastic collisions.

The displacement efficiency is taken as 0.8, and assumed independent of the energy of the PKA energy, the irradiated material or the irradiation temperature. This irradiation dose is measured in terms of displacements per atom (dpa), with the dose rate expressed in terms of displacements per atom per second (dpa/s). All discussion of irradiation damage made in this thesis will be expressed in these terms.

\(^{5}\) The term Frenkel pair is used to describe the vacancy-interstitial atom mixed dumbbell complex.
The primary knock-on atom, or PKA for short, is the atom that is struck by the irradiating neutron. The PKA will be knocked out of its regular lattice location. It will then proceed to interact with other atoms within its immediate vicinity. This ultimately causes a chain reaction of atoms being knocked out of their original lattice sites. However, as the process occurs, the amount of energy that each subsequent atom has decreases, until ultimately no further atoms are knocked out of their regular lattice locations. At the end of the process, an number of atoms may remain in an interstitial locations, i.e. locations that lie between the interstices of the crystal lattice. These atoms are termed self-interstitial atoms, or SIA's. The formation of these SIA's by neutron interaction is shown schematically in Figure 2.6.

![Cascade core](image)

**Figure 2.6: Schematic of neutron irradiation induced defects in a bcc material**

The self-interstitial atom is vital to the mechanisms of solute segregation during irradiation, which is discussed in considerable detail in Chapter 6. More detailed discussion of irradiation damage to crystalline materials has been written by Kelly[15]. Additionally, this process, termed the damage cascade, has been modelled with some success by Bacon and co-workers[16] and by Heinisch and Singh[17], using Monte Carlo-type modelling techniques. These models predict the damage that an energetic neutron causes in a regular lattice structure. These models generally need huge amounts of computing power, owing to the billions of calculations that are performed. Typically, the duration of such a damage cascade event is of the order of pico-seconds ($10^{-12}$ seconds). More recently, these models have incorporated effect of grain boundaries in the damage cascade, with some success. These displacement cascade Monte Carlo simulations are not considered in this Thesis, although an atomistic simulation to predict grain boundary segregation is introduced in Chapter 8.
2.3.3 Void Swelling

Void swelling, or irradiation swelling, is an increase in volume, and hence decrease in density, caused by the formation of voids containing inert fission gases. This increase in volume could lead to many engineering problems, owing to the increase in size of components. Similarly, the decrease in density could lead to changes in mechanical properties, such as strength and fatigue resistance. Thermal conductivity may also change, which could be critical in core applications.

In reactor structural materials, such as stainless steel, void swelling is typically due to helium. In contrast, the fuel pins usually made of zirconium suffer void swelling due to the presence of gases such as krypton ($^{85}$Kr) and xenon ($^{133}$Xe). An example of the formation of helium is the irradiation of nickel, shown below. Irradiating nickel, having a mass of 58, with an energetic neutron causes the nickel atom to become excited. Following another neutron reaction, the nickel becomes more excited. Finally, it emits a helium atom, and becomes nickel with a mass number of 56.

\[ ^{58}\text{Ni} \rightarrow {^4n} \rightarrow ^{59}\text{Ni}^* \rightarrow {^4n} \rightarrow ^{56}\text{Fe} \]

Following this initial void formation, a process of vacancy-assisted growth then occurs. This growth is due indirectly to interstitials, which can move more freely through the lattice structure. These mobile interstitials are removed at a greater rate than vacancies by the dislocation network within the structure. This causes an excess of vacancies within the material, which combine with the voids initiated by the helium, causing void growth.

The effect of void swelling is an increase in material volume, accompanied by a decrease in density, which typically occurs at temperatures around half of the melting temperature of the material. It is prominent in the structural elements of many commercial reactors, where the materials are experiencing severe radiation damage, often up to 40 dpa per year at temperatures in the range of 500-600°C. Measured swelling for such material has been as high as 10%. The consequence of such swelling is the reduction in strength of the components, which could lead to buckling and possibly failure of the component. Dimensional enlargement of components such as fuel rods may mean that they become difficult to remove from the reactor.

2.3.4 Irradiation Assisted Stress Corrosion Cracking (IASCC)

In broad engineering terms, stress corrosion cracking is a failure mechanism due to both trans- and inter-granular cracking that involves the presence of both an induced stress field and a corrosive environment. Many stainless steels are susceptible, although they are materials that are generally thought to be resistant to many forms of corrosive attack. In these situations, the protective coating of the stainless steel has been broken down or removed, causing the localised corrosion of the material in regions that have become sensitised in some way. Sensitisation in stainless steels occurs along grain boundaries when
the material is cooled from high temperatures. Upon cooling, chromium carbides form along
the grain boundaries, causing a reduction in the level of chromium along these boundaries.
These boundaries are thus termed sensitised, since they have a reduced resistance to
chemical attack. Further details of sensitisation can be found in general metallurgical texts,
for example, Honeycombe and Bhadeshia\cite{18}, Smallman\cite{19} and Lula\cite{20}.

Associated to some extent with segregation (which will be discussed in considerable
detail later), IASCC occurs due to a weakening of the grain boundaries of the material such
that they become susceptible to stress corrosion cracking. This weakening can be attributed
to segregation, and particularly the depletion of Chromium in austenitic stainless steels, such
as Type 316. However, the process of IASCC is somewhat complex. During prior thermal
processing, grain boundaries become enriched with Chromium. Under irradiation conditions,
the Chromium present at the grain boundaries diffuses back into the grain matrix, causing a
Chromium depleted region immediately adjacent to the grain boundary. A more in-depth
study of this phenomenon can be found in the PhD thesis of Colin Goodwin\cite{21} and recently
published papers surrounding this work\cite{22,23}.

2.3.5 Irradiation hardening and embrittlement

The phenomena of irradiation-induced hardening and embrittlement are of
particular concern when selecting material for use in reactor pressure vessels. The purpose
of the vessel is to maintain integrity during operation of the reactor. In event of a meltdown
of the reactor core, the pressure vessel must remain intact to prevent any spreading of
radioactive particles. If the reactor pressure vessel becomes weakened during service, there
may be a possibility that the integrity of the vessel could be compromised during an
emergency. Typically, the steels that are used in the construction of RPV's are ductile. This
means that prior to complete failure, the material will exhibit plastic deformation. This
deformation is due to the movement of dislocations within the lattice of the metal. However,
if the movement of these dislocations is impeded somehow, then the material becomes
brittle. Brittle failure is typically along grain boundaries and cleavage planes within the lattice
of the metal.

Most metals exhibit a ductile to brittle transition temperature. At high
temperatures, it is possible for dislocations to move easily. However, as the temperature is
lowered, these dislocations become trapped and are unable to move. The material will
therefore not be able to plastically deform under stress. The Ductile to Brittle Transition
Temperature (DBTT) graph shown in Figure 2.7 shows the effects of both irradiation and
post-irradiation annealing on the behaviour of a Fe-1.6Ni-0.007P-0.06Cu RPV steel\cite{24}. It can
be seen that irradiation causes the upper shelf energy of the specimens to fall. In the work,
this was attributed to the segregation of phosphorus to grain boundaries, an effect that will
be covered in considerable detail in the bulk of this thesis. The increase in the upper shelf

energy during post irradiation annealing was assumed to be due to the removal of phosphorus from the grain boundaries.

Figure 2.7: Irradiation induced change to DBTT (from Gurovich and co-workers\textsuperscript{(24)})

The ductile to brittle transition temperature therefore needs to be constantly monitored, since this temperature gives an indication of the material's state of ductility or brittleness. A ductile material will exhibit high impact energy, since energy is required to induce plastic deformation by moving dislocations within the material. Brittle materials, conversely, have low impact energies, since the material is unable to plastically deform and failure occurs along grain boundaries and other cleavage paths.

Figure 2.8: Davidenkov's diagram (from Gurovich and co-workers\textsuperscript{(24)})

The phenomena of embrittlement and hardening are due to the energetic neutron flux creating new dislocations within the material. Thus, the production of a super-saturation of point defects causes an increase in the hardness of the material by physically introducing dislocations. The high dislocation density increases the hardness of the steel by impeding slip.
and movement of dislocations. As the irradiation dose increases, the dislocation density increases, causing the yield strength and ultimate tensile strength of the steel to increase, eventually saturating with the yield strength approaching the ultimate tensile strength.

The effect of radiation hardening of materials can be shown by the Davidenkov diagram, shown schematically in Figure 2.8. The diagram plots yield stress against temperature for both un-irradiated and irradiated samples, and highlights simply any shift in the ductile to brittle transition temperature.

2.3.6 Thermal and irradiation-assisted creep

Creep is a phenomenon that can occur in materials, whether under irradiation or purely thermal conditions, which are in a state of stress. It is a phenomenon that engineers are concerned with where materials are operating at temperatures that are greater than half of the absolute melting temperature of the material, although it does occur at lower temperatures, be it far slower.

Thermal creep is associated with the movement of dislocations, and manifests itself in three stages. Primary, or transient, creep starts rapidly, but slows towards the secondary, steady state stage. Dislocations can easily overcome barriers to their movement, thus plastic deformation is rapid. However, work hardening occurs as dislocations begin to pile-up at interfaces such as grain boundaries, and the rate of plastic deformation slows. This is the final, tertiary stage of thermal creep.

Study of activation energies show that irradiation creep is a process connected with the migration of interstitials. The reasoning for this is that the migration energy of irradiation-created interstitials is less than that of vacancies. Irradiation enhanced creep, as summarised by Garner[23], can be described by four distinct regimes.

1. Transient primary: An initially high creep rate, which decelerates to a steady state.
2. Steady state secondary in absence of swelling: A state maintained so long as no void swelling occurs. The rate of this creep is higher than the corresponding thermal creep rate at that temperature.
3. Swelling enhanced creep: In this regime, the onset of swelling marks an increase in the creep rate. The rates of swelling and creep are related in this region.
4. Feedback dominated, or disappearing creep: The feedback from the increasing swelling begins to reverse, which in turn begins to reduce the rate of irradiation creep until a state is attained where swelling occurs in the absence of creep. This phase is followed by material failure.
Experimentally, irradiation enhanced creep has been shown to occur in many RPV structural materials\textsuperscript{[9]}. In addition, irradiation creep has also been observed in graphite and zirconium\textsuperscript{[26]}. The results have also indicated that the rupture time of irradiated samples is far shorter than that of thermally aged materials. However, it must be noted that the degree of enhancement of creep is greatest for lower irradiation temperatures, since at higher temperatures, the effects of thermal creep take over.

There exist a number of irradiation enhanced creep models. The most commonly discussed are Stress Induced Preferential Absorption of defects (SIPA) and Stress Induced Preferential Nucleation of defects (SIPN). A thorough description of these models for irradiation assisted creep can be found in the review paper by Matthews and Finnis\textsuperscript{[26]}. However, in order to illustrate the complexity of the effects that are occurring, Figure 2.9 shows the relationships that exist between the SIPA approach to irradiation assisted creep and the dislocation density of the material.

![Figure 2.9: Relationship between various dislocation and creep mechanisms during irradiation (from Matthews and Finnis\textsuperscript{[26]})](image)

**2.4 Chapter summary**

In this Chapter, a brief discussion of nuclear power has been presented, highlighting the different approaches to producing electricity from the current technology of fission and the future technology of fusion. Some of the materials used in the construction of these reactors have been introduced and their various properties discussed. A short summary of the various phenomena that occur within these materials during continued exposure to irradiation has also been made. It is hoped that reader now has an insight into the complexity of nuclear reactor engineering, together with how varied the solutions are to the problems that arise owing to the effects of irradiation on technological alloys.
Chapter 3: Analytical techniques

3.1 Introduction

Current technological advances have meant that there are now several techniques of examining microstructural features within materials. The techniques themselves are widely varying, from sample preparation, through examination method, to data collection. The discussion presented here will compare and contrast the various processes relevant to this thesis. It is hoped that the reader will gain an understanding of the terminology used for the different techniques, as well as an indication of the relative merits of each technique. In subsequent Chapters, reference will be made to the various techniques mentioned here in relation to work performed by various research groups. It is hoped that the reader will then be in a position to be able to draw their own conclusions regarding the techniques that researchers utilise.

For a more thorough description of the techniques described here, there are many well-written texts available. For example, the series of texts by Williams[27-30] cover many aspects of transmission electron microscopy, and the book by Watt[31] provides good descriptions of many electron microscopy techniques. Other useful texts include Flewitt and Wild[32] and Buseck and co-workers[33].

3.2 Fundamentals of microscopy

Prior to discussing the various techniques used in the analysis of materials, a brief description of some of the fundamentals of microscopy will be made. The basic phraseology of microscopy will be introduced so that the subsequent sections of this chapter may be read with a clearer understanding of the phenomena that are occurring and being examined during the material analysis procedure. Initially, a description of basic optical metallurgical microscopy will be presented. This will be followed by a description of the merits of using electron beams instead of light beams to examine microstructures.

3.2.1 Resolution

The most common question asked about a microscope is how much can it magnify a sample. An alternative, and more accurate way, of asking this question is what can it resolve, or what is the smallest separation between objects that the microscope can distinguish. The basic equation defining the resolution of any microscope, be it optical or electron beam, is Abbe's equation. It can be expressed as:

\[ d_0 = \frac{0.61\lambda}{n \sin \alpha} \quad (3.1) \]

where:
- \( d_0 \) is the minimum observable separation between two features
- \( \lambda \) is the wavelength of the illuminating source
n is the refractive index of the medium through which the illumination is passing
α is the semi angle of the beam that is illuminating the source

For a light microscope, with an objective lens magnification of 40x, using white light, the maximum theoretical resolution in air is 0.5μm. In a typical light microscope, the lenses are marked in terms of magnification, since the actual theoretical resolution is never really approached in simple light microscopes owing to factors such as imperfections in the lens systems.

3.2.2 Electron wavelength

Examination of Abbe’s equation for resolution shows that changing the wavelength, the angle of incidence of the illuminating beam and using a different viewing medium all change the resolution obtainable from a microscope. In optical microscopy, there are limits on both the angle of beam incidence, and the viewing medium. These factors in turn limit the resolution of the microscope. However, it was noticed that electrons exhibit both wave- and particle-like properties. Of interest to microscopists is the wavelength of electron beams. It was shown by de Broglie that the wavelength of an electron beam could be determined from the following relationship:

\[ \lambda = \frac{h}{mv} \]  (3.2)

where:
λ is the electron beam wavelength
h is Planck’s constant
m is the mass of the electron
v is the velocity of the electron.

Since the kinetic energy of an electron is known to be \( \frac{1}{2}mv^2 \), which in turn is equal to Ve (where V is the applied voltage and e is the charge on the electron), de Broglie’s relationship can be re-written as:

\[ \lambda = \frac{1.23}{\sqrt{V}} \]  (3.3)

Therefore, for a 50keV electron, the wavelength, \( \lambda \), is equal to 0.0055nm. Incorporating this figure into Abbe’s resolving power relationship shows that a resolution of 0.0024nm is theoretically possible.

---

1 A beam passing through a system of lenses which is focussed to a point will be conical, and thus there will be a minimum angle of the tip of the cone.
3.2.3 Lens imperfections

So far, it has been shown that the theoretical resolution of electron microscopes is orders of magnitude higher than for optical microscopes, owing to the shorter wavelength of electron beams. However, the figures presented for resolution are purely theoretical, and therefore assume a perfect instrument. However, in all microscopes, the lens system will contain imperfections. In optical systems, these imperfections will lie in the glass lenses that are used. However, electron microscopes cannot use glass lenses in the same way as optical systems, and have to use lenses that bend the electron beam. The types of lenses that can be used can be categorised as either magnetic or electrostatic.

The types of defects that occur in lens systems in electron microscopes can be broken down into the following classifications:

- Chromatic and spherical aberration
- Astigmatism
- Distortion

Chromatic aberrations are due to the electron beam containing electrons with a range of energies. In electron systems, this effect cannot be totally eliminated. In light microscopy, on the other hand, the light source can contain light of all the same wavelength by using either an achromat or an apochromat.

Astigmatism is caused by the electron deflecting fields produced in the lenses not being perfectly symmetrical about the lens axis. This causes the lens to have different focal lengths in different orientations. This effect can be corrected for, by using a device known as a stigmator. This device can independently vary the direction and magnitude of the compensating field to allow for the lens imperfection.

Distortion in electron microscopes generally only occurs when the microscope is being operated at relatively low magnifications, and results in barrelling, pin cushioning or spiralling of the observed image. These effects are due to either the radial change in magnification across the image field, or the variation in image rotational angle with radial distance from the optic axis.

3.2.4 Probe size, current and brightness

The X-ray and electron counts necessary for either EDXS or EELS detectors are determined by the local foil thickness and the image probe current, I, which can be calculated from the following relationship.

\[ I = \frac{\pi^2 \alpha^2 d^2 \beta_s}{4} \]  

(3.4)

where:

- \( \alpha \) is the probe convergence semi-angle
- \( d \) is the probe diameter
- \( \beta_s \) is the source brightness.
The image probe current will vary with distance from the centre of the beam. This distribution of beam current can be seen in Figure 3.1. Commonly, workers quote electron beam probe sizes as either Full Width, Half Maximum (FWHM). Some workers may quote Full Width, Tenth Maximum (FWTM). These data can be used to quickly compare the accuracy of subsequent analysis techniques.

![Figure 3.1: Schematic of full width, half maximum (FWHM) and full width, tenth maximum (FWTM)](image)

This equation does not, however, take into any account spherical aberration (caused by the probe-forming lens) and diffraction by the final aperture. These two effects give rise to a disc of confusion, which effectively limits the current in a probe. Thus, the equation can be re-written to take into account these effects.

\[
I_{\text{max}} = \frac{32\pi^2 \beta_s}{16} \left( \frac{e^{8/3}}{C^2} - \frac{4}{3} (1.22\lambda)^2 \right)
\]

where:  
- \( C_s \) is the spherical aberration coefficient of the lens.  
- \( \lambda \) is the electron wavelength.  
- \( d \) is the probe diameter.

Thus, for a fixed optical system, the only variable is the source brightness, \( \beta_s \). Source brightness, \( \beta_s \), is a function of the type of source and the beam accelerating voltage. It is defined as the current density per unit solid angle, and can be defined from the equation derived by Langmuir in 1937 as follows.

\[
\beta_s = \frac{AT^2 e^{-\phi/kT}}{\pi} \left( 1 + \frac{V}{kT} \right)
\]

where:  
- \( V \) is the accelerating voltage.  
- \( A \) is a constant (theoretically 120 amp cm\(^{-2}\) K\(^{-2}\) for pure metals).  
- \( \phi \) is the work function of the metal in electron volts.  
- \( k \) is Boltzmann’s constant.  
- \( T \) is the absolute temperature.
For a field emission gun source as found in a typical FEGSTEM, $\beta \sim 10^9$ amps/cm$^2$/sr$^2$ at 50keV, whereas for a heated lanthium hexaboride (LaB$_6$) source, $\beta \sim 5 \times 10^6$ amps/cm$^2$/sr. The brightness obtainable from a FEG, combined with its small spot size, mean that its spatial resolution is far superior to any other type of electron microscope. Even so, against this advantage of a field emission source is the requirement for a very high vacuum of $10^{-9}$ to $10^{-10}$ mbar for stable operation of the cold field emitter. A simple tungsten filament requires a vacuum of $10^{-3}$ torr or better, and a LaB$_6$ filament requires a vacuum in the order of $10^{-7}$ torr. This means that the cost of a FEGSTEM is much higher than that of a simple thermionic TEM with a separate scanning unit.

Probe diameter, $d$, is a parameter often quoted, but without being carefully defined, and is rarely measured accurately. Studies have shown that it is possible to produce probes for which 80% of the total current is contained within a diameter of less than 1nm. In this case, the total current was in the region of $10^{-10}$ amps.

### 3.2.5 Electron beam sources

In the previous section, the various parameters that govern the suitability of electron sources to imaging samples were discussed. The following sections will describe the three sources that are utilised in electron microscopy. For comparison, data relating to the three types of electron beam source can be found in Table 3.1.

<table>
<thead>
<tr>
<th>Source</th>
<th>Brightness (A cm$^2$ sr$^{-1}$)</th>
<th>Stability (%)</th>
<th>Source size</th>
<th>Energy spread (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten</td>
<td>$3 \times 10^5$</td>
<td>$\sim 1$</td>
<td>50$\mu$m</td>
<td>3</td>
</tr>
<tr>
<td>LaB$_6$</td>
<td>$3 \times 10^6$</td>
<td>$\sim 2$</td>
<td>1$\mu$m</td>
<td>1</td>
</tr>
<tr>
<td>Cold field emission</td>
<td>$10^9$</td>
<td>$\sim 5$</td>
<td>5nm</td>
<td>0.5</td>
</tr>
<tr>
<td>Thermal field emission</td>
<td>$10^9$</td>
<td>$\sim 5$</td>
<td>5nm</td>
<td>2</td>
</tr>
</tbody>
</table>

**Table 3.1. Data comparing the various electron beam sources.**

### 3.2.5.1 Conventional thermionic tungsten hairpin source

This is the most common type of electron beam source found in electron microscopes. The hairpin is heated to a temperature of 2800K by direct resistance heating. The surrounding Wehnelt cylinder, together with the anode which is held at earth, act as an electrostatic lens, which focuses the image of the filament at a point just beyond the anode. This causes the electron beam to be very stable. The source size is around $50\mu$m, and at an operating condition of 100keV gives a source brightness of $3 \times 10^5$ A cm$^2$ sr$^{-1}$. In a modern electron microscope, this type of source gives a probe size with a diameter of 40nm and a current of 1nA. In a Scanning Transmission Electron Microscope (discussed later) this would

---

2 One steradian (sr) is subtended at the centre of a sphere of radius $r$ by a portion of its surface of area $r^2$. Thus, 1 sphere = $4\pi$ sr.
be reduced to a probe size of 4nm with a current of 0.05nA. An image of a tungsten-hairpin filament source is shown in **Figure 3.2**.

![Image 3.2: Conventional tungsten wire electron gun filament](image)

### 3.2.5.2 Lanthium hexaboride (LaB₆) source

The main advantage of using a LaB₆ source is the increased lifetime of the source. Typically, a LaB₆ source will have a brightness of \(10^7\) A cm\(^{-2}\) sr\(^{-1}\) at 100keV, which is an improvement of a factor of 30 over a conventional thermionic tungsten hairpin source. However, if this source brightness is reduced to only a factor of 10 over a tungsten filament, the lifetime of the source can be increased to around 1000hours, roughly 10 times that of a tungsten filament. A typical LaB₆ source is shown in **Figure 3.3**.

![Image 3.3: Lanthium hexaboride (LaB₆) electron beam source](image)

### 3.2.5.3 Field Emission Gun

As mentioned earlier, the field emission gun is a replacement for a standard thermionic electron source which gives much a much higher beam brightness, which in turn increases the image probe current. Thus, for a small probe size, there will still be sufficient
current to provide enough data for chemical composition analysers, such as EDXS or EELS. The electric field at the surface of the tip of a field emitter is proportional to the square of its radius, thus most field emitters are manufactured from etched needlepoint single crystal tungsten wires, usually in the <111> crystal orientation. An example of a field emission gun source is shown in Figure 3.4. However, the effect of having such a high field around the source is that there may be short-term instabilities in emission current. To avoid this problem it is necessary to run the source in a very high vacuum in order to prevent the tip becoming too contaminated. Even so, the tip will need to be ‘flashed’ occasionally to remove any absorbed impurities. The actual emitting region of a field emission tip is in the region of 10nm across, compared to 50-100μm of the crossover of a typical thermionic emission tungsten hairpin source. A schematic layout of a field emission gun can be seen in Figure 3.5, showing the position of the anodes and the electron source.

Figure 3.4: Field emission electron source

Figure 3.5: Schematic diagram of electrode arrangement in a field emission gun.
3.2.6 Beam broadening

It has been shown that electron beams can be obtained with probe sizes of less than 1nm. This does not mean, however, that it is possible to image samples with this resolution. Transmission electron microscopy relies on the sample being examined to be electron invisible. Ideally, this would mean a sample that is one atomic plane thick. This is not the case. Scanning electron microscopy images samples by scanning a beam across their surface, and detecting electrons and X-rays that are emitted by the sample. Again, ideally, this would occur from the uppermost atomic layer of the sample.

Due to the beam interacting with the sample, a situation termed beam broadening occurs. This can be seen schematically for various sample geometries in Figure 3.6. As the beam penetrates the sample, the electrons are deflected from their original paths. The beam effectively enlarges. This means that x-ray and electron emissions from the sample are obtained from a region that is larger than the probe size. This effectively reduces the resolution of the microscope.

Figure 3.6: Schematic of electron beam spreading within samples.

An approach to determining the degree of beam broadening in samples has been presented by Faulkner and co-workers[34]. This approach was tailored to determining the effect of probe size on the measured segregation of an element at a grain boundary or similar interface. The work showed that the beam broadening varied linearly with sample thickness.

3.3 Transmission Electron Microscope

The use of electron beams in order to increase resolution of microscopes has been discussed in some detail. Essentially, a Transmission Electron Microscope (commonly abbreviated to TEM) is a compound light microscope using an electron beam as its illumination system. However, the use of electron beams also enables the generation of many signals from the sample. Figure 3.7 shows the various signals that are generated when an electron beam interacts with a sample. In all, it can be seen that there are potentially seven signals that can be used for analysis.
Figure 3.7: Photon and charged particle emission phenomena that take place at an electron-bombarded surface

It is possible to operate the TEM in many modes. These modes are used to obtain different information from the sample. The most commonly used modes are bright field and selected area diffraction. Schematically, their ray diagrams can be seen in Figure 3.8. Bright field illumination permits the viewing of the sample, using the same lens arrangement as a light microscope. Selected area diffraction (SAD) is useful for determining the structure of the sample. The image obtained is a pattern of dots, which can be interpreted to give the crystal structure of the sample as well as data regarding the lattice size.

Subsequent chapters of this thesis discuss various aspects of the phenomenon of segregation, both experimentally and theoretically. Experimentally, segregation can be measured using various techniques of electron microscopy. The magnitude of segregation varies between alloys, and can range from a few nanometres to tens or hundreds of nanometres. Therefore, the highest resolution microscopes are the best tools to use, since they will be able to analyse small regions of the material to gain the best data.

In order to use these techniques to measure segregation across an interface such as a grain boundary, it is necessary to determine the chemical composition at various points across the interface. As mentioned earlier, the type of data obtainable from either system is due to the type of detectors fitted to the equipment. Thus, chemical composition can be determined in one of two ways. Firstly, by the counting the number of X-rays given off, as in energy dispersive spectroscopy (EDS or EDXS), or secondly, by the counting the number of electrons given off, as in electron emission loss spectrometry (EELS). These two types of chemical analysis are described later in this section.
3.3.2 Data collection in TEM systems

The use of electron microscopy to detect segregation within alloys has been mentioned. With reference to Figure 3.7, many signals are emitted from samples when illuminated by an electron beam. The detection of these signals gains valuable microstructural data pertaining to the structure of chemistry of the sample. The following sections will describe the main systems that are used in TEM systems, namely energy dispersive spectroscopy and electron energy-loss spectrometry.

3.3.2.1 Energy dispersive spectroscopy (EDS or EDXS)

This technique of x-ray analysis uses a semi-conductor detector to classify x-rays according to energy rather than wavelength. The detector converts the energy of the incident x-ray photons into pulses of current, proportional to the x-ray energy. These pulses are then amplified and fed, typically, into a computer program that manipulates the data into a more usable type. The total energy range that may be covered by an EDXS system would be between 10 and 80 keV. The energy range of 1 to 10 keV is particularly useful. This range covers the $K_\alpha$ lines of elements with atomic weights of 11 to 32, the $L_\alpha$ lines of elements with atomic weights of 30 to 80, and the $M$ lines of elements with atomic weights from 62 upwards.
The detector used is a single crystal disc of lithium-doped silicon (Si(Li)), with dimensions of 3-5mm thickness and a detecting area for TEM applications of around 30mm². This large detecting area is so that it will pick up very weak signals from very small area of the sample. The detecting apparatus is an obvious addition to a TEM, since the detector needs to be cooled by liquid nitrogen, and thus a 'bottle' supplying the liquid N₂ will be attached to the TEM. These bottles typically provide up to one week's supply of liquid N₂.

The detector itself is mounted on the end of a 'snout', which is inserted through the column of the TEM so that the detector can 'see' the sample. No focusing of the detector is required. However, the detector needs to be placed in a position so that it absorbs as many of the generated X-rays as possible. Currently, efficiencies of collection of 2% can be expected from most EDXS systems.

At the end of the detector is a beryllium window. The purpose of this window is to prevent the liquid N₂-cooled detection crystal from icing over with any condensable vapours present in the TEM. However, this beryllium window, although very thin (typically 7.5μm thick), does reduce the sensitivity of the detector to very low-energy X-rays. This therefore places a lower limit on the detection of most EDXS systems of sodium (atomic number = 11) and upwards.

However, should the electron column of the TEM be sufficiently 'clean', it is possible to use EDXS detectors with either no windows, or a less absorbent window than the beryllium system described. These windowless, ultra-thin window (UTW) or super atmospheric thin window (SATW) systems have increased sensitivity over the beryllium-window detector system described.

### 3.3.2.2 Electron energy-loss spectroscopy (EELS)

Electron energy-loss spectroscopy is an alternative technique to EDXS for measuring RIS profiles. However, only a few microscopes have the necessary apparatus to perform this technique. The technique relies on the energy lost by an electron when it produces a characteristic X-ray. The spectrum of energies of transmitted electrons contains discontinuities at the ionisation edges, which can be used to derive chemical composition. This can be seen graphically in **Figure 3.9**. However, the technique is limited by specimen thickness, and is most useful for determination of light elements, typically sodium and below. EELS also has an advantage over EDXS in that it has a much higher collection efficiency, typically in the region of 50%, compared to around 2% for EDXS. However, the method of collection is much slower than for EDXS, and sometimes requires up to 100 seconds, since the signal to background count ratio is much poorer and the energy levels are detected sequentially. An improvement over this is PEELS, which is discussed later.
A typical EELS spectrum consists of three distinct regions. Firstly, and most dominantly, is the zero loss peak. This spectrum is composed firstly of electrons that have not been scattered by the specimen, secondly of electrons that have suffered phonon scattering, and thirdly of electrons that have been elastically scattered. The energy width of the zero-loss peak is an addition of the energy spread of the electron source and the energy resolution of the spectrometer. The second region of an EELS spectrum is made from electrons that have excited plasmons, and this region extends up to about 50eV loss. It is the third region of the spectrum that is of importance, since this provides the data of the characteristic ionisation losses.

The third region consists of a continuous background count, onto which the characteristic ionisation losses are superimposed. Analysis of these losses is made simply by measuring the energy associated with each loss and comparing it to tabulated energies. By comparing the shape of the edges, it is also possible to determine the chemical state of the element being analysed.

### 3.3.2.3 PEELS detectors

As mentioned earlier, EELS detectors take a long time to collect data, since the energy levels are measured sequentially. An improvement to this method is to measure all energy levels at the same time. This is Parallel Electron Energy Loss Spectrometry, or PEELS. The time taken to perform an analysis is therefore much reduced over conventional EELS.
3.4 Dedicated FEGSTEM

The first example of a FEGSTEM was produced by Crewe in 1971. The illumination was provided by a cold tungsten point, from which electrons were extracted by the strong electric field between it and a suitably positioned electrode. This basic configuration has been retained over the years, and in current FEGSTEM's the final spot diameter can be in the region of 0.5nm. Even with such a small spot size, however, it is still necessary to produce a large enough number of X-ray or electron counts for the detectors to pick up in order to determine local chemical composition. This is especially true for thin film samples, such as those used in FEGSTEM analysis. When an electron beam interacts with a bulk sample, the beam spreads, as shown previously in Figure 3.6. This beam spreading means that the X-ray emitting volume becomes larger than the original spot size. However, for thin film samples, the beam does not spread as much, and thus there is a smaller volume of material for the X-rays to be emitted from. In order to obtain a large enough X-ray count, it is necessary to use an electron beam with a large current density. It is for this reason that FEGSTEM's are particularly useful for microanalysis.

![Schematic layout of a dedicated FEGSTEM](image)

Figure 3.10: Schematic layout of a dedicated FEGSTEM

The most common usage of STEM covers the scanning attachment to a dedicated TEM, which enables the finely focused electron probe to scan across the sample. Results can be obtained from as many different operating modes as there are detectors fitted, such as detectors for secondary, back-scattered and transmitted electrons and X-rays.
An alternative approach is the dedicated STEM, typically in the form of a Field Emission Gun - STEM (FEGSTEM) in which a Field Emission Gun is used as the source of the electron beam. These types of electron microscopes are dedicated to obtaining near-atomic resolution in materials that would otherwise give little or no contrast. Again, the results obtainable from such a piece of equipment is determined by both the number and type of detectors fitted to the machine. However, the spatial resolutions of these dedicated FEGSTEM's are far better than those obtainable from 'piggy-back' STEM's. This point will be discussed in more detail later.

### 3.5 Auger electron spectroscopy (AES)

The discussion so far has concentrated on the various techniques of transmission electron microscopy. This section will discuss a dedicated system of detecting Auger electrons that are emitted from samples during electron beam analysis. Auger emission by samples in an electron beam is another means of elemental identification. The Auger electron is the result of a secondary process following the removal of an electron from an inner shell by the incident electron beam as shown in Figure 3.11. The process can be described as follows.

- An incident electron beam causes the ejection of an inner shell electron, such as from the K shell.
- An L shell electron falls into this newly created K shell vacancy, emitting a K X-ray photon.
- This K photon is absorbed into the L shell, causing the ejection of an L shell electron. This is the Auger electron.
- The two vacancies in the L shell are then filled by electrons from the M shell, which in turn is followed by the emission of L X-ray photons.

The analysis of the Auger electron can be performed by a spectrometer, and typically, this can analyse elements with atomic weights of two or over. There are two different types of spectrometer used for collecting Auger electrons. These are the Cylindrical Mirror Analyser (CMA) and the hemispherical analyser with a transfer lens (HSA). Both the transfer lens and the analyser are electrostatic lenses, and the voltages used are typically less than 1kV.

Owing to the nature of the process, in that it is a secondary occurrence, the electrons emitted will only come from the uppermost layers of atoms in a sample, typically as few nanometres from the surface. The process must therefore be performed in a high-vacuum chamber, with high current densities of the Incident beam so that a high signal-to-noise ratio is obtained.
If it is possible to raise the current density high enough, it is possible to perform Scanning Auger microscopy. However, raising the current density will reduce the spatial resolution of the microscope unless a field emission source is used.

3.6 Field ion microscopy

The development of the field ion microscope started in 1937 by Muller[31]. This early apparatus, actually termed the Field Emission Microscope (FEM), used a sample in the form of a pointed wire. This was held within an evacuated spherical vessel, which has a fluorescent coating on its internal surface. A potential difference of several kV was set up between the sample and the sphere. This caused electrons to be emitted from the sample tip, which travelled in a radial direction to the imaging surface. The magnification could therefore be calculated from the ratio of the sample tip radius to the radius of the imaging sphere. It was possible to obtain magnifications of one million times.

This early system lacked the ability to resolve individual atomic sites, although it did give an indication of the crystal structure of the sample. The original field emission set-up held the sample at a negative potential relative to the imaging sphere. Muller found that by reversing this potential and maintaining a low pressure of inert gas within the vessel, it was possible to resolve individual atomic sites. The use of the imaging gas meant that the image of the sample was made up from positive gas ions, which were created at the sample tip. This development was the first field ion microscope (FIM).
The field ion microscope has been used for metallurgical characterisation on the atomic scale for many years. In contrast to the techniques described in previous sections, this method of analysis does not rely on an electron beam to either generate an image of the sample, or induce an emission of a characteristic X-ray or electron. Schematically, the apparatus required are shown in Figure 3.12. Note that the chamber is no longer spherical in shape. Additionally, the samples are cooled to cryogenic temperatures to assist with the controlled ionisation at the surface of the sample.

![Figure 3.12: Schematic of field ion microscope](image)

The samples are needle-shaped and have hemispherical tips, which have radii in the range of 0.01 to 0.1μm. The imaging gases used are typically helium or neon. An image of the specimen tip is then displayed on a phosphor screen by the projection of the ionised gas atoms onto this screen. An example of the output obtained can be seen in Figure 3.13. By

![Figure 3.13: Example of output obtained from FIM](image)
controlling the rate at which the surface atoms of the sample are removed, it is possible to gain an indication of how the structure of the material changes with depth. This is particularly useful for examining precipitates and internal interfaces, such as grain boundaries and dislocation structures.

3.6.1 Atom probe field ion microscopy (APFIM)

The atom probe field ion microscope was introduced in 1968 that made possible the identification of different species of atoms. The development that allowed this was the atom probe microanalyser. The analysis is performed by examining the mass-to-charge ratio of atoms that are removed from the surface of the sample. The concept has continued to evolve from these early stages, and has now reached a point where the resolution has reached around 1nm, together with full elemental identification.

An Atom Probe typically consists of two main components.

- A Field Ion Microscope in which near atomic resolution images of the surface of the specimen are obtained
- A mass spectrometer in which the elemental identity of selected atoms may be obtained.

In order to identify the elemental concentrations within the sample, the mass spectrometer is used. An example of this type of apparatus is the Oak Ridge National Laboratories (ORNL) energy-compensated atom probe field ion microscope (APFIM). The mass spectrometer of this instrument incorporates a Poschenrieder-type electrostatic lens to compensate for small differences in the energies of the ion field evaporated from the specimen. This effectively improves the mass resolution of the APFIM a by a factor of around 10 times that of instruments without this lens. The mass resolution now attainable is \( m/\Delta m > 2500 \). For the older generation non-energy-compensated instruments, \( m/\Delta m \sim 250 \), and prior to that, the imaging atom probe (IAP) and position sensitive atom probe (PoSAP) had mass resolutions in the range of 30 to 50. This instrument has been used to perform many characterisations of reactor pressure vessels by the research group of Mike Miller[35–38]. The results obtained from these papers will be discussed in some detail in relation to segregation behaviour in subsequent chapters.

3.7 Other systems of electron microscopy

The discussion has highlighted the main systems of electron microscopy that are of use in determining segregation within samples. Additionally, many other systems warrant a few words of description.

High Voltage Electron Microscopes (HVEM) are a generation of TEM systems that utilise exceedingly high accelerating voltages. Voltages above 500 kilovolt are common,
although mega-volt microscopes do exist. The use of HVEM systems is aimed at examining thicker specimens. Typical samples used in standard TEM systems are nanometres thick, whereas when using a HVEM, samples as thick as 10 microns can be used. Although thicker samples can be used in standard 100kV TEM machines, electron scattering within the sample causes the image to lose sharpness. The use of very high electron-beam energies avoids this problem, as there is a lower probability that the electrons will be scattered within the sample.

The use of high voltage electrons can also irradiate samples and produce damage that is comparable to that produced by energetic neutron irradiation. Typically, the energy of electrons required is in the order of MeV, compared to the keV microscopes that are commonly used to analyse samples. Using this technique of irradiation has the benefit that the time period required to irradiate the samples is low. Another advantage of the technique is that it is possible to select the area that is to be irradiated. This allows the operator to select an area of interest and analyse its behaviour during irradiation. The phenomenon of grain boundary migration is therefore observable. A particularly interesting paper involving this technique of sample irradiation and analysis is that of Mahon and co-workers\textsuperscript{39}.

\textbf{3.8 Chapter summary}

The aim of this Chapter was to introduce the various techniques that are available to analyse grain boundary composition, and to compare their relative merits. From the information presented, it would appear that the most suitable method of grain boundary analysis is the use of a FEGSTEM, with either EDXS or EELS chemical composition analysis attachments. This approach would also allow the determination of elemental concentration profiles away from the interface, which the technique of Auger Electron Spectrometry does not easily permit. This method also has the advantage over AES in that it is possible to select the interface to be studied. AES is reliant on the intergranular fracture of the material being analysed. This fracture process may therefore preferentially select the grain boundaries that are exposed, and may not give a representative analysis.

The other method presented was that of Atom Probe Field Ion Microscopy. This technique could be compared to FEGSTEM since it is possible to generate concentration profiles for regions of the material away from grain boundaries. However, the procedure of specimen preparation is considerably more difficult than that required for FEGSTEM analysis. The APFIM specimen requires a suitable grain boundary to be located in the tip of a sharp needle, with a tip radius of in the order of 0.1 \textmu m.

Thus, it can be summarised that FEGSTEM would appear to be the ideal technique to obtain elemental concentration data from grain boundary regions. The spatial resolution is suitably high, the specimen preparation is relatively straight forward, and the samples are not damaged as they are in the techniques of AES and APFIM.
Chapter 4: Material characterisation

4.1 Introduction

In Chapter 2, the materials usage in nuclear reactors was discussed, together with an introduction to the wide range of deleterious processes that occur within the microstructure of the various materials during continued irradiation. An introduction to the experimental techniques of how we can analyse the materials in order to gather useful information was presented in Chapter 3. This Chapter will give details of the materials that have been considered for the theoretical work that will be presented later in this Thesis.

The first section of this Chapter will detail the compositions of the materials, together with their prior-to-service thermal histories. These thermal histories arise due to the manufacturing processes that have been employed in the construction of the reactor pressure vessel. The subsequent sections will present a range of experimentally obtained results. These will give details of the microstructure of the material, focussing on the grain boundary composition arising due to both the thermal history and the subsequent reactor service conditions of temperature, neutron dose and dose rate.

4.2 Material classification and manufacture

The material being considered for the work of this Thesis is a ferritic manganese molybdenum low-alloy steel, classified as ASME SA533B, class 1. This particular alloy classification is commonly used in the construction of reactor pressure vessels used in pressurised water reactors, discussed in Chapter 2. The chemical compositions of the alloys under consideration are shown in Table 4.1 in terms of weight percent. In all, four different alloys are considered, each with slightly differing composition, prior-to-service thermal history and irradiation conditions.

<table>
<thead>
<tr>
<th>Element</th>
<th>SF</th>
<th>SG</th>
<th>SP</th>
<th>SL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.048</td>
<td>0.051</td>
<td>0.062</td>
<td>0.062</td>
</tr>
<tr>
<td>Mn</td>
<td>1.46</td>
<td>1.50</td>
<td>1.58</td>
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<tr>
<td>Mo</td>
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<td>0.48</td>
<td>0.52</td>
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<tr>
<td>Si</td>
<td>0.48</td>
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<tr>
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<td>0.023</td>
<td>0.017</td>
</tr>
<tr>
<td>Cr</td>
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<td>0.044</td>
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<td>0.005</td>
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<td>&lt;0.005</td>
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<td>0.024</td>
<td>0.002</td>
<td>0.01</td>
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<tr>
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<td>0.010</td>
<td>0.014</td>
<td>0.018</td>
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<tr>
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<td>&lt;0.002</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
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<tr>
<td>S</td>
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<td>0.024</td>
<td>0.0135</td>
<td>0.013</td>
</tr>
<tr>
<td>Ni</td>
<td>0.25</td>
<td>0.31</td>
<td>0.063</td>
<td>0.087</td>
</tr>
</tbody>
</table>

Table 4.1: Material composition (wt.%) of the alloys examined
The models described in later Chapters in this Thesis consider the concentration of the elements in terms of atom fraction. The figures presented in Table 4.1 therefore need to be converted into these units. The atomic percent content of the main elements of the alloys are presented in Table 4.2.

<table>
<thead>
<tr>
<th>Element</th>
<th>SF</th>
<th>SG</th>
<th>SP</th>
<th>SL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.22</td>
<td>0.24</td>
<td>0.28</td>
<td>0.29</td>
</tr>
<tr>
<td>Mn</td>
<td>1.48</td>
<td>1.52</td>
<td>1.59</td>
<td>1.65</td>
</tr>
<tr>
<td>Mo</td>
<td>0.28</td>
<td>0.28</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>P</td>
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<td>0.03</td>
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<tr>
<td>Cu</td>
<td>0.21</td>
<td>0.42</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>Ni</td>
<td>0.24</td>
<td>0.29</td>
<td>0.06</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 4.2: Concentration (at.%) of key elements in alloys

These alloys can be classified more simply. Carbon contents are typically between 0.2 and 0.3 at.%. Phosphorus contents are between 0.03 and 0.04 at.%. Nickel contents are approximately 0.3 at.% for alloys SF and SG, and are lower at approximately 0.08 at.% for alloys SP and SL. Alloy SG has the highest copper content, around 0.4 at.%, compared to the other alloys. Therefore, alloy SG can be termed high-copper, high-nickel, and alloy SF can be termed intermediate-copper, high-nickel. Alloys SP and SL are very similar, both containing low copper and nickel. Of these two alloys, alloy SL has less phosphorus.

4.2.1 Reactor pressure vessel construction

The material being considered in this work is taken from the shell cylinder that is part of a PWR RPV. Within the vessel are four thermal shields, constructed of Type 304 stainless steel. Additionally, type 308L is used as the internal cladding of the shell in order to protect the RPV from excessive irradiation.

The shell cylinder is comprised of two shell plates, welded longitudinally together. Since these shell plates are approximately 150 mm thick, the welding process used is multi-layer submerged-arc. Following welding, the cylinder is post weld heat treated at 600°C for 6 hours. The cylinder is then examined, and any repair welds are made. The cylinder is then heat-treated. Following heat treatment, the cylinder is shot blasted, machined and inspected. The cylinder is then clad internally with 308L stainless steel, again by submerged arc welding.

The cylinder assembly is then stress relieved by heating firstly to 300°C at 25°C per hour, and then to 600°C at 50°C per hour. Following assembly of the cylinder, the RPV is then completed. The shell cylinder head assembly is welded to the cylinder, with the welds stress relieved. The thermal shields are attached within the vessel, and finally the shell forging is welded in place. Again, weld stress relieving is performed at 600°C. In total, the vessel is subjected to a number of stress relieving operations, all performed at 600°C. The total duration of these processes is 41.5 hours.
4.2.2 Post-weld heat treatment simulation

The description of the RPV manufacturing process given here highlights the complexity of the operation. Overall, a number of stress-relieving processes are performed at 600°C, and as has just been mentioned, these total approximately 42 hours. It is therefore possible to simulate these stress-relieving operations by a simpler heat treatment process, such as that shown in Figure 4.1. The heat treatments do, however, vary slightly between alloys, although for the purposes of theoretical modelling, the heat treatment presented will only be considered.

Phase 1: Heat to 920°C, hold for 6 hours and then water spray quench (146°C/hr to below 300°C)
Phase 2: Heat at 47°C/hr to 601°C, temper (1) for 41.5 hrs at 601°C, cool at 23°C/hr to below 300°C
Phase 3: Heat at 50°C/hr to 651°C, temper (2) for 6 hrs at 651°C, cool at 38°C/hr to below 300°C

Figure 4.1: Simulated post-weld heat treatment process of RPV steel
4.3 Analysis of un-irradiated samples

The un-irradiated material has been examined at lower magnifications using straightforward optical microscopy. Higher magnification examination of the grain boundaries has been performed using TEM/FEGSTEM. Analysis of the grain boundary regions of the samples has been performed using FEGSTEM with EDXS, together with AES. The procedures used and results obtained will be presented in the following sections.

4.3.1 Optical analysis

Material was taken from machined Charpy specimens and mounted in bakelite, and then ground, polished and etched. The grinding and polishing was performed manually to a final grade 1 micron. Etching was performed by submerging the samples in a 2% Nital solution for between 15 and 20 seconds to expose the grain boundary structure. Optical micrographs of Alloy SF obtained from an MEF-3 microscope using a tungsten filament illumination source are shown in Figures 4.2 to 4.4. The photos shown are at magnifications of 10x, 20x and 50x. Reproduction of the micrographs has increased these magnifications by a further 1.4 times.

The microstructure can be most easily observed in highest magnification micrograph in Figure 4.4. It can be seen that a range of grain sizes exist in the material, and there does not appear to be any preferential geometry. The grain sizes would appear to range from 50 microns up to approximately 300 microns. Additionally, the grain boundaries would appear to be decorated with small precipitates. These have been imaged further using the higher magnification that is obtainable using FEGSTEM.

Figure 4.2: Optical micrograph of Alloy SF (magnification 14x)
Figure 4.3: Optical micrograph of Alloy SF (magnification 28x)

Figure 4.4: Optical micrograph of Alloy SF (magnification 70x)
4.3.2 TEM and FEGSTEM analyses

A number of samples of the RPV alloys were analysed using both TEM and FEGSTEM. The TEM used was the JEOL 100CX facility at Loughborough University. The Vacuum Generators HB601 FEGSTEM that was used for detailed grain boundary analysis is located at the Department of Mechanical and Materials Engineering at Liverpool University. This FEGSTEM is equipped with detectors for both EDXS and EELS analysis, allowing compositional analysis of grain boundaries, together with approximate sample thickness determination. The analyses were performed both by experienced technicians and by the author under close supervision, owing to the sensitivity of the apparatus.

4.3.2.1 Sample preparation

Thin wafers of material were taken from samples SF025, SP81, SG144 and SL168 from regions up to 5mm either side of the notch of the Charpy samples supplied by Rolls Royce and Associates. These wafers were in the region of 170-200microns thick and were cut using a STRUERS precision saw. From these wafers, 3mm disks suitable for mounting in TEM/FEGSTEM holders were then manually punched. These disks were then manually ground until thicknesses in the region of 50 to 100 microns were obtained. The disks were then electro-jet polished until a perforation was observed.

The electro-jet polishing was performed using a STRUERS TENUPOL electropolisher using an electrolyte solution of 10% perchloric acid, 20% glycerol and 70% methanol, held at a constant temperature of -15°C. Using this technique ensured that the samples were prepared uniformly and with as little mechanical deformation as possible. This method also ensures that the perforation and the adjacent electron-invisible material is centrally-located in the sample. The disks were then stored in phials of AR grade ethanol to prevent them from corrosion and deteriorating.

4.3.2.2 Sample examination

Each prepared disk was subsequently examined using TEM in order to determine its suitability for further examination in the FEGSTEM. Disks that exhibited suitably large thin areas around the perforation, together with several visible, well-oriented grain boundaries were kept for further analysis. The samples were subsequently transferred to Liverpool University for analysis.

The samples were mounted in a Beryllium sample holder that had a fixed 10° tilt angle and examined individually in the FEGSTEM, owing to the lack of a carousel stage for multiple samples. This sample holder aimed the samples towards the EDXS detector so that a higher X-ray count rate could be obtained. However, this meant that subsequent alignment of grain boundaries was difficult, and thus any grain boundaries that were observed could not be perfectly aligned with the electron beam. Once a sample was mounted in the sample holder, it was then placed into the FEGSTEM, which was then evacuated to a pressure of $10^{-9}$
This process took up to 1 hour to complete, and where possible the samples were mounted in the previous day to provide a more stable sample. In cases where the sample was mounted the previous day, there was little or no drift of the sample when being examined. However, some samples that were mounted in the FEGSTEM immediately prior to being examined did show signs of drift when being examined. This introduced errors into the readings, since the area of analysis was continually wandering. In order to keep this to a minimum, the beam was corrected every 30 seconds whilst data was being collected.

Additional errors to the data stemmed from the fact that the material is magnetic, and thus caused the beam to become astigmatic. To keep this to a minimum, the samples needed to be as thin as possible. However, owing to the use of the TENUPOL in the preparation of the samples, a ridge of material was often formed around the perforation, and simply by removing this ridge, the problem could be solved.

Two methods of examination were employed. The method used for the majority of the readings was the spot analysis technique, where the electron beam was aimed at the region of interest. However, this technique was reliant on the grain boundary being well-focussed, and that the beam drifted as little as possible. Where the beam did drift, the beam was corrected every 30 seconds, as mentioned earlier. This technique is particularly useful when building up a segregation profile across a grain boundary since it is possible to step the beam across the boundary.

In cases where the grain boundary was ill defined, and alternative approach was adopted. In these situations, a box was highlighted around the area of interest and the beam was allowed to raster through this box. Thus, data could be collected from within the entire box. This technique would give values of absolute segregation over the width of the box. Thus, readings needed to be collected from a region covering the grain boundary and from regions away from the grain boundaries in order to give a comparison of the two results. This approach, however, results in very diluted concentrations unless the magnification is sufficiently high that analysis of a length of oriented boundary is possible. Only results obtained from grain boundary spot analyses are presented in this Chapter.

Examples of the types of micrograph obtained from the analyses are shown in the following figures. Figures 4.5 and 4.6 show an area of sample SF025 in both bright and dark field illumination. The grain boundary can be seen to be well aligned between the precipitates shown. Additionally, the dark field micrograph shows the grain boundary within the precipitates. The precipitates shown are approximately 200nm in length. Figure 4.7 is a higher magnification micrograph of the region between the precipitates. A precipitate is located at the centre of the grain boundary. The dislocation structure can also be seen to differ between either side of the grain boundary. However, this can be attributed to the difference in the crystal orientation of the two grains, which causes a different orientation of dislocation to be observed, due to the invisibility criteria. Figure 4.8 is a micrograph of a
particularly well oriented grain boundary in alloy SG. **Figure 4.9** shows a micrograph of the pile up of dislocations adjacent to a grain boundary precipitate in Alloy SP.

**Figure 4.5:** FEGSTEM bright field micrograph of sample SF025 showing grain boundary precipitates

**Figure 4.6:** FEGSTEM dark field micrograph of sample SF025 showing same grain boundary region
Figure 4.7: FEGSTEM dark field micrograph of sample SF025 at higher magnification than Figure 4.6

Figure 4.8: FEGSTEM micrograph of sample SG168 showing a well defined and oriented grain boundary
4.3.2.3 EDXS results

The grain boundary concentration results obtained from the FEGSTEM/EDXS point analyses performed at Liverpool University are shown in Table 4.3. The figures presented are the concentrations of the elements phosphorus, manganese and molybdenum, which will be used to compare with the theoretically predicted values later in this Thesis.

The results show considerable variation in the grain boundary concentrations, both between alloys and between grain boundaries within the same alloy. For example, phosphorus enrichment varies from 0.03 to 0.2wt.% in alloy SG, from 0.07 to 0.27wt.% in alloy SF, and from 0.02 to 0.25wt.% in alloy SP. Only two suitably aligned grain boundaries were analysed in alloy SL, and of these, one exhibited no phosphorus at all.

The results for both manganese and molybdenum also show considerable spread. For manganese, the results typically lie between 0.7 and 1.5wt.%, although alloy SF only exhibited 0.56wt.% on one grain boundary, and alloy SG exhibited 1.79wt.%. For manganese, there is more variation between the alloys, with the lowest concentration observed in alloy SG of only 0.12wt.%, and the highest concentration of 2.24wt.% observed in alloy SF.
Table 4.3: GB concentrations of P, Mo and Mn (wt.%) from Liverpool FEGSTEM/EDXS analyses

The material has also been analysed using a dedicated FEGSTEM facility at Harwell. The grain boundary concentrations obtained from EDXs analysis are presented in Table 4.4 for Alloys SP and SG. The data show the mean concentration, together with the minimum and maximum concentrations observed, expressed in terms of percentage monolayer coverage. The conversion from percentage monolayer coverage into atomic percent is taken from Beere[40]. This assumes that 1 monolayer of phosphorus is equal to 25 atomic percent. It is worth noting here also that it is likewise assumed that 1 monolayer of carbon is assumed to be equal to 40 atomic percent. The converted figures are presented in Table 4.5, again showing minimum, mean and maximum.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phosphorus</th>
<th>Manganese</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF025 #01</td>
<td>.07</td>
<td>1.03</td>
<td>1.05</td>
</tr>
<tr>
<td>SF025 #05</td>
<td>.15</td>
<td>.56</td>
<td>1.11</td>
</tr>
<tr>
<td>SF025 #10</td>
<td>.07</td>
<td>1.01</td>
<td>.7</td>
</tr>
<tr>
<td>SF025 #13</td>
<td>.13</td>
<td>1.16</td>
<td>2.24</td>
</tr>
<tr>
<td>SF025 #17</td>
<td>.27</td>
<td>.68</td>
<td>1.57</td>
</tr>
<tr>
<td>SF025 #26</td>
<td>.09</td>
<td>1.54</td>
<td>1.06</td>
</tr>
<tr>
<td>SP81 #15</td>
<td>.02</td>
<td>.85</td>
<td>.6</td>
</tr>
<tr>
<td>SP81 #19</td>
<td>.25</td>
<td>.85</td>
<td>.86</td>
</tr>
<tr>
<td>SP81 #20</td>
<td>.23</td>
<td>.79</td>
<td>.75</td>
</tr>
<tr>
<td>SP81 #25</td>
<td>.14</td>
<td>1.48</td>
<td>1.6</td>
</tr>
<tr>
<td>SL152 #1</td>
<td>.08</td>
<td>.69</td>
<td>1.01</td>
</tr>
<tr>
<td>SL152 #6</td>
<td>-</td>
<td>1.01</td>
<td>.68</td>
</tr>
<tr>
<td>SG168 #1</td>
<td>.03</td>
<td>1.79</td>
<td>.6</td>
</tr>
<tr>
<td>SG168 #2</td>
<td>.2</td>
<td>1.53</td>
<td>.74</td>
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<tr>
<td>SG168 #5</td>
<td>.04</td>
<td>1.06</td>
<td>.55</td>
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<td>SG168 #13</td>
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<td>.98</td>
<td>.51</td>
</tr>
<tr>
<td>SG168 #16</td>
<td>.1</td>
<td>.77</td>
<td>.72</td>
</tr>
</tbody>
</table>

Table 4.4: Harwell FEGSTEM/EDXS results of un-irradiated samples expressed in percentage monolayer coverage

<table>
<thead>
<tr>
<th>Sample</th>
<th>GB P (monolayer%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
</tr>
<tr>
<td>SP72</td>
<td>0</td>
</tr>
<tr>
<td>SG33</td>
<td>2</td>
</tr>
<tr>
<td>SL</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.5: Harwell FEGSTEM/EDXS results of un-irradiated samples expressed in terms of atomic percent

<table>
<thead>
<tr>
<th>Sample</th>
<th>GB P (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
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<tr>
<td>SP72</td>
<td>0</td>
</tr>
<tr>
<td>SG33</td>
<td>0.5</td>
</tr>
<tr>
<td>SL</td>
<td>-</td>
</tr>
</tbody>
</table>
It was mentioned earlier that the grain boundaries of the alloys appeared to exhibit significant quantities of precipitates. During the FEGSTEM/EDXS analysis of the samples, it was found that these precipitates were carbides containing significant proportions of manganese and molybdenum. A number of these precipitates were analysed in alloy SG, and the concentrations of phosphorus, manganese and molybdenum are shown in Table 4.6. These precipitates were analysed as it was found that the material adjacent to the grain boundaries contained considerably less manganese than the bulk concentrations indicated. This can be seen from Figures 4.10 and 4.11, which show a number of point analyses performed along a line perpendicular to a grain boundary in alloys SF and SP. These figures indicate that the bulk material contains between 0.5 and 0.8% manganese, which is considerably less than the 1.5% originally quoted. The bulk figure of the molybdenum would appear to be slightly less than the 0.5% quoted. Examples of the EDXS spectra obtained from these point analyses are shown in Figures 4.12 and 4.14, showing both matrix and grain boundary results.

<table>
<thead>
<tr>
<th>Sample reading</th>
<th>Phosphorus</th>
<th>Manganese</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG168 #9</td>
<td></td>
<td>14.33</td>
<td>3.07</td>
</tr>
<tr>
<td>SG168 #10</td>
<td>.03</td>
<td>1.65</td>
<td>73.14</td>
</tr>
<tr>
<td>SG168 #11</td>
<td>.05</td>
<td>42.27</td>
<td>1.01</td>
</tr>
<tr>
<td>SG168 #12</td>
<td></td>
<td>7.21</td>
<td>30.64</td>
</tr>
<tr>
<td>SG168 #17</td>
<td></td>
<td>1.69</td>
<td>76.50</td>
</tr>
<tr>
<td>SG168 #18</td>
<td></td>
<td>1.23</td>
<td>35.99</td>
</tr>
<tr>
<td>SG168 #21</td>
<td>-</td>
<td>1.33</td>
<td>38.89</td>
</tr>
<tr>
<td>SG168 #22</td>
<td>.05</td>
<td>39.98</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.6: Compositions of precipitates (wt.%) found in alloy SG

![Graph](image)

Figure 4.10: Point analyses performed across grain boundary in sample SF025
Figure 4.11: Point analyses performed across grain boundary in SP81

Figure 4.12: EDXS analysis of Sample SF showing traces for grain boundary composition and matrix composition
Figure 4.13: EDXS analysis of Alloy SF showing traces for both grain boundary and matrix composition

The analyses presented in Figures 4.10 and 4.11 were obtained from point analyses performed at a number of points on a line perpendicular to the grain boundary. This analysis technique was used in a number of samples owing to drift. In order to correct the drift, the analysis was stopped every 30 seconds of the total 300 seconds that it took. It was then possible to check that the beam was still located over the correct location. In those samples were negligible drift was observed, it was possible to perform automated linescans across well aligned boundaries. The results of three such linescans are shown in Figures 4.14 to 4.16. The concentration profile across each boundary is shown, together with an image of the boundary being analysed. However, this procedure is still limited, since only qualitative data is obtained, although it is possible to determine the width of the segregated zones adjacent to the grain boundary.
Figure 4.14: Link analytical digital line scan across grain boundary in Alloy SF
Linescan length = 31.79 nm

Figure 4.15: Link analytical digital line scan across grain boundary in Alloy SG
Figure 4.16: Link analytical digital line scan across grain boundary in Alloy SG
4.3.3 AES analysis

A number of samples were analysed using an Auger spectroscope at the Interface Analysis Centre and Bristol University. The technique of Auger has been discussed in Chapter 3, and has been shown to be a particularly valuable tool in determining grain boundary compositions to a high degree of accuracy. Since the sample is fractured and examined whilst being contained within a vacuum system, contamination of the fracture surface is kept to a minimum. However, the technique does rely on the intergranular (brittle) fracture of the samples in order to expose the grain boundaries. Samples are therefore fractured at low temperature, having been cooled in liquid nitrogen. The fracture surface can then be examined using the instruments scanning attachment in order to find suitably aligned and exposed grain boundaries. However, should the material fail in a ductile manner and not expose any grain boundaries, analysis is virtually impossible.

In subsequent Chapters, it will be seen that many observations of grain boundary segregation are made using the technique of AES. Some of these observations will also incorporate depth profiling of the segregation. This technique is performed by sputtering the sample, i.e. removal of surface layers from the sample. Since the rate of sputtering typically is quite slow, it is possible to obtain fine-scale profiles of segregation in the vicinity of grain boundaries. In the work performed here, this final technique could not be performed. The reasons for this will become apparent.

4.3.3.1 Sample preparation

Samples corresponding to the geometry shown in Figure 4.17 were machined, ensuring that the material of interest, i.e. the weld material, was located at the notch in the sample. The number of samples machined totalled eight, comprising of two samples each from four different alloys, namely SG100, SL387, SP37 and SF36. The composition of these four alloys has been presented in Table 4.1.

The work was performed using a JEOL JAMP 30 Scanning Auger Microprobe (SAM). Each sample was mounted in the fracture stage of the SAM, which was then evacuated to a pressure of less than 10^-7 Pa. The samples were cooled to liquid nitrogen temperature (77K) and held at this temperature for 1 hour prior to fracturing. The samples were then moved from the fracture stage of the SAM to the imaging stage, maintaining the correct vacuum pressure, and were then analysed.

Figure 4.17: Schematic of the sample used for Auger examination
4.3.4.2 Results

It was found that the samples fractured primarily in an intragranular (through the grains) manner instead of an intergranular (along the grain boundaries) manner. This meant that there were few suitably aligned and exposed grain boundaries to analyse. The results obtained from the samples tested are presented in Table 4.7. The results indicate which particular sample of each alloy the result corresponds to, together with the grain boundary concentrations, presented in atomic percent. These figures have subsequently been calculated in terms of enrichment ratios, and are shown in Table 4.8.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample</th>
<th>Normalised Atomic Percent</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>SG100</td>
<td>A</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>78.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>74.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>75.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>72.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>66.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>72.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>78.0</td>
</tr>
<tr>
<td>SL387</td>
<td>A</td>
<td>98.0</td>
</tr>
<tr>
<td>SP37</td>
<td>A</td>
<td>74.0</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>75.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>73.0</td>
</tr>
<tr>
<td>SF36</td>
<td>A</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>74.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>77.0</td>
</tr>
</tbody>
</table>

Table 4.7: Grain boundary concentrations (at.%) obtained by AES

<table>
<thead>
<tr>
<th>Material</th>
<th>Enrichment (CblCa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
</tr>
<tr>
<td>SG100</td>
<td>30.2</td>
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<tr>
<td></td>
<td>53.5</td>
</tr>
<tr>
<td></td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td>30.2</td>
</tr>
<tr>
<td></td>
<td>44.2</td>
</tr>
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<td></td>
<td>34.9</td>
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<td></td>
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<td></td>
<td>46.5</td>
</tr>
<tr>
<td>SL387</td>
<td>30.0</td>
</tr>
<tr>
<td>SP37</td>
<td>97.6</td>
</tr>
<tr>
<td></td>
<td>87.8</td>
</tr>
<tr>
<td></td>
<td>78.0</td>
</tr>
<tr>
<td>SF36</td>
<td>53.7</td>
</tr>
<tr>
<td></td>
<td>85.4</td>
</tr>
<tr>
<td></td>
<td>53.7</td>
</tr>
</tbody>
</table>

Table 4.8: Enrichment ratios of elements
4.4 Irradiated samples  
A number of the alloys have been irradiated, using the now decommissioned reactor
called HERALD at Aldermaston. The irradiation parameters of dose, dose rate and
temperature are shown in Table 4.9. All of the samples, with the exception of sample
SL152, were irradiated at 255°C. This sample was irradiated at the slightly higher
temperature of 315°C. The irradiation dose rates vary considerably between the samples,
with a range of between $6.3\times10^{-9}$ and $8.9\times10^{-11}$ dpa/s. It is worth noting that alloy SG had samples irradiated at three different dose rates within this range. The irradiation dose that the samples experienced ranged from 1.5 to 38 mdpa.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose (mdpa)</th>
<th>Flux (dpa/s)</th>
<th>$T_{irr}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP65</td>
<td>38</td>
<td>$6\times10^{-9}$</td>
<td>255</td>
</tr>
<tr>
<td>SG25</td>
<td>1.5</td>
<td>$8.9\times10^{-11}$</td>
<td>255</td>
</tr>
<tr>
<td>SG02</td>
<td>12.34</td>
<td>$6.4\times10^{-10}$</td>
<td>255</td>
</tr>
<tr>
<td>SG35</td>
<td>29</td>
<td>$6\times10^{-9}$</td>
<td>255</td>
</tr>
<tr>
<td>SL152</td>
<td>26.62</td>
<td>$6.3\times10^{-9}$</td>
<td>315</td>
</tr>
</tbody>
</table>

Table 4.9: Irradiation conditions

The irradiated samples were then analysed by FEGSTEM/EDXS at Harwell. The phosphorus grain boundary concentration results obtained from the analysis are shown in Table 4.10. These data are presented in terms of percentage monolayer coverage. As with the un-irradiated samples, these have been converted into terms of atomic percent by taking the assumption of Beere\(^{[40]}\) that 1 monolayer of phosphorus is equal to 25 atomic percent. The converted data are shown in Table 4.11.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GB P (monolayer%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min.</td>
</tr>
<tr>
<td>SP65</td>
<td>6</td>
</tr>
<tr>
<td>SG25</td>
<td>3</td>
</tr>
<tr>
<td>SG02</td>
<td>11</td>
</tr>
<tr>
<td>SG35</td>
<td>0</td>
</tr>
<tr>
<td>SL152</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 4.10: Grain boundary phosphorus segregation results from irradiated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>GB P (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min.</td>
</tr>
<tr>
<td>SP65</td>
<td>1.5</td>
</tr>
<tr>
<td>SG25</td>
<td>0.75</td>
</tr>
<tr>
<td>SG02</td>
<td>2.75</td>
</tr>
<tr>
<td>SG35</td>
<td>0</td>
</tr>
<tr>
<td>SL152</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4.11: Grain boundary phosphorus segregation results from irradiated samples
4.5 Chapter summary

This Chapter has presented a range of experimental results that have been obtained from analysis of a range of RPV steel samples. The grain boundary phosphorus data obtained from the FEGSTEM and AES techniques can be used to compare with the theoretical predictions of thermally induced segregation, since the samples have been post-weld heat treated. The models used to determine the theoretical values of thermally induced segregation will be presented in the following Chapter. The data obtained from Harwell for the irradiated samples can be used to compare with the radiation-induced segregation model, which will be introduced in Chapter 6. An overall discussion of these results, together with comparison with the theoretical predictions will be presented in Chapter 9.
Chapter 5: Thermally induced segregation

5.1 Introduction

Segregation of alloying and impurity elements within a technological alloy is a complex phenomenon. In its simplest form, elemental segregation can be termed as a compositional difference that exists between regions of the same grain. However, the mechanisms by which individual atoms, be they either alloying elements or impurity elements, segregate to grain boundaries are varied. This Chapter will discuss the area of Thermally Induced Segregation (TIS). The thermal effects that induce segregation could be either a constant temperature ageing, or a rapidly changing temperature, such as would occur when a material is quenched. These two thermal effects are possibly the most common processes that engineering materials are subjected.

![Interfacial segregation diagram]

Figure 5.1: Mechanical and kinetic materials phenomena involving segregation (from Hondros and Seah[41])

If a welded component is considered, the material will be subjected to rapidly fluctuating temperatures during the welding process. Reactor pressure vessels are commonly tens of centimetres thick. In order to weld such thick sections of metal, the technique of submerged metal arc welding is employed. Welding metal in the order of 20cm thick would therefore require tens of weld passes. The material in the heat-affected zone adjacent to these weld zones would therefore be subjected to many thermal cycles.
In many cases following welding, a heat treatment process is employed. These treatments involve heating the entire component to a predetermined temperature, and then holding the component at this temperature for a period of time. The selection of temperature and time are dependent upon the material properties that are required, such as strength, ductility, grain size and so on.

Thermally induced segregation will occur in many alloy systems due to manufacturing processes such as those that have been mentioned here. There is therefore a need to know what drives this effect. This would enable more accurate forecasting of materials properties, and would therefore enable engineers to increase the lifetime and safety of critical reactor components. The various affects of segregation on mechanical properties are summarised in Figure 5.1. This Chapter will discuss the broad subject area of thermally induced segregation, dividing it into Thermal Equilibrium Segregation (TES) and Thermal Non-Equilibrium Segregation (TNES). Under these two headings, a discussion of both prior experimental and theoretical work will be presented. Theoretical models to predict the behaviour of both TES and TNES will be introduced, and predictions made for the alloys under consideration in this Thesis.

5.2 Thermal equilibrium segregation

In many low alloy steels, tempering in the range of 500 to 650°C followed by quenching can cause the material to become embrittled. This phenomenon is widely known as Reversible Temper Embrittlement (RTE), since it can be alleviated by tempering at a temperature lower than 500°C. The effect can be most easily demonstrated by performing notched-bar impact testing on alloys tempered at different temperatures. The results show the lowering of the upper shelf energy and a corresponding increase in the ductile to brittle transition temperature (DBTT) of those samples tempered at temperatures between 500 and 650°C. Examining the fracture surfaces of the samples will also show that the fracture mode has changed from being primarily transgranular in nature to primarily intergranular.

Most work in this area has used the technique of Auger Electron Spectroscopy (AES) to determine the elemental composition at the grain boundaries. This technique, as discussed in Chapter 3, is particularly suitable to analysing fracture surfaces, since the Auger electrons are emitted from zones very close to the surface of the sample. However, in order to expose suitable grain boundaries, the samples must first be cooled to temperatures that induce brittle, and therefore intergranular, fracture. The fracturing of the sample must also be performed within a closed-system under vacuum conditions in order to prevent any contamination of the exposed fracture surface. Recalling the experimental work presented in Chapter 4, the samples were cooled to cryogenic temperatures, i.e. cooled in liquid nitrogen. Even at this low temperature, brittle fracture of the samples is not guaranteed, and the
exposed fracture surface needs to be carefully examined to find suitably exposed and oriented grain boundaries.

It has been found that RTE is due to the segregation of alloying and impurity elements to the grain boundaries, causing the net reduction of the cohesive strength of the grain boundary. The alloy elements that segregate have been classified as those elements found in the IV to VI groups in the Periodic Table, which are shown below in Table 5.1.

<table>
<thead>
<tr>
<th>Group IV</th>
<th>Group V</th>
<th>Group VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>N</td>
<td>O</td>
</tr>
<tr>
<td>Si</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>Ge</td>
<td>As</td>
<td>Se</td>
</tr>
<tr>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi</td>
</tr>
</tbody>
</table>

Table 5.1: Elements from Groups IV to VI in the periodic table

The degree of segregation of the impurity element appears to increase both with Group number and with Period number. Thus, elements from Group VI would segregate more than those elements found within Group IV. Likewise, within Group V, bismuth (Bi) would be expected to segregate more than nitrogen (N). However, the inclusion of other metallic elements in the alloy system will affect both the degree of segregation of these elements together with the magnitude of embrittlement that the material exhibits.

Manganese, for example, reduces the solubility of the Group VI chalcogen elements (sulphur (S), selenium (Se) and tellurium (Te)) in iron by precipitation, for example MnS\(^{[42]}\). This has the effect of reducing the magnitude of the segregation of these highly segregating elements to the grain boundaries. There would thus appear to be some sort of co-segregation of elements occurring within alloys systems. The final element of this group in oxygen, and although it would be expected to segregate to grain boundaries, it in fact cannot since its solid solubility is very low.

The aim of this section is to discuss and contrast the experimental work that has been performed that analyses grain boundary segregation of phosphorus and other elements. The work that has been performed modelling the effect of segregation of single elements within binary alloy systems will follow, since this is the most simplified aspect of discussing equilibrium segregation. From this basis, it will be possible to introduce the various theories for site competition and non-competitive co-segregation. For a more general discussion of the subject, the reader is referred to the review paper written by Hofman and Lejcek\(^{[43]}\).

5.2.1 Experimental observations of RTE

There has been considerable work performed to examine the thermal equilibrium segregation of alloying and impurity elements in steel alloys. The discussion presented here will firstly highlight work that has examined the effect of bulk concentration and ageing temperatures on phosphorus segregation behaviour. Following this introduction, a discussion
of the experimental work that has examined more complex alloy systems will be presented. This discussion will cover interactions between phosphorus and other alloying elements, such as carbon, molybdenum and manganese, together with how these interactions affect the segregation behaviour of the elements. The discussion will introduce the phenomenon of grain boundary site-competition that has been shown to occur in certain alloy systems. The techniques used to obtain these experimental observations will also be highlighted for comparison with the work performed for this thesis.

5.2.1.1 Observations of phosphorus segregation

Recent results from examination of pure binary alloys are rare. However, there do exist some observations of phosphorus equilibrium segregation in Fe-P alloy steels. Erhart and Grabke(44) examined an essentially binary Fe-P alloy prior to looking at the segregation of other alloying additions. These observations are discussed in the following section. The samples analysed were annealed for a range of times, at temperatures between 400 and 800°C. Following this process, the samples were placed in the ultrahigh vacuum system of an Auger Electron Spectroscope, which operated at a pressure of 1.3x10⁻⁸Pa. The samples were cooled to -120°C and fractured. There exposed fracture surfaces were then examined using the technique of AES.

![Figure 5.2: Equilibrium grain boundary segregation of phosphorus plotted as a function of bulk content at constant temperature(from Erhart and Grabke(44))](image)

The results obtained showed that for samples annealed at 500°C, the grain boundary enrichment of phosphorus increased as the bulk content of phosphorus increased. This relationship in the results is shown in Figure 5.2. They also found that for phosphorus bulk concentrations of over 0.1wt.% the boundaries appeared saturated with phosphorus atoms. This grain boundary saturation has been termed 'monolayer coverage', and many
results are presented expressing grain boundary concentrations as fractions of monolayer coverage. At the other end of the scale, they reported that segregation was observed in alloys with phosphorus bulk contents as low as 0.003 wt.%. In addition to demonstrating the effect of bulk content on the grain boundary concentration of phosphorus, Erhart and Grabke also demonstrated the effect of temperature on the segregation of phosphorus in α-iron. The results obtained from the analysis can be seen in Figure 5.3, and indicate the relationship between P concentration and temperature. This relationship is higher equilibration temperatures cause the grain boundary concentration to decrease. This effect is shown to occur over a range of bulk contents, between 0.003 wt.% and 0.33 wt.% phosphorus.  

![Figure 5.3: Grain boundary concentration of phosphorus plotted as a function of equilibrium temperature for P contents (from Erhart and Grabke)](image)

Mackenbrock and Grabke examined the segregation of phosphorus in a 12Cr-Mo-V steel, doped with 0.057% phosphorus and aged at 450, 550 and 600°C for times up to 10,000 hours. The samples were analysed using AES, having been cooled to -120°C prior to being fractured under vacuum conditions. Their results indicated that the grain boundary concentration decreased with increasing temperature and decreasing bulk concentrations. It was shown that at an ageing temperature of 600°C, the grain boundary concentration reaches a saturation level at around 1000 hours of ageing, as shown in Figure 5.4. However, at lower ageing temperatures, the grain boundary concentrations did not appear to reach a saturation level.
Figure 5.4: Kinetics of grain boundary segregation of phosphorus in 12Cr-Mo-V steel aged at different temperatures (from Mackenbrock and Grabke\textsuperscript{[45]})

Their results also indicated that phosphorus became trapped at dislocations, and that phosphorus segregated prevalingly to high-angle prior austenite grain boundaries. The effect of the dislocations was to trap the phosphorus and remove it from solution within the material, therefore lowering the amount of phosphorus available to segregate. This trapping effect was therefore assumed to lower the equilibrium level of segregated phosphorus at the grain boundaries. The effect of dislocations, although shown to be significant in this work, tends to be somewhat neglected in much of the literature surrounding phosphorus segregation. The reason for this is the importance of examining the behaviour of grain boundaries when impurity element segregation is occurring, owing to the embrittlement that accompanies the effect. However, when discussing radiation-induced segregation in Chapter 6, the importance of dislocations within the material will become evident.

5.2.1.2 Simultaneous segregation of multiple elements

The previous section illustrated work that had concentrated on the effects of concentration, ageing temperature and ageing time on the segregation behaviour of phosphorus. No consideration was made of the effect that different alloying elements might have on the segregation behaviour of phosphorus. This section will highlight a range of work that has been performed to investigate these varying effects.

The Fe-P binary alloy analysed previously by Erhart and Grabke\textsuperscript{[44]} was further analysed to determine any effect due to carbon. The Fe-P alloys were carburised in flowing \( \text{CH}_4-\text{H}_2 \) mixtures at 600°C, which gave carbon contents between 10 and 75 wt-ppm. The samples were then further aged at 600°C to promote segregation of both phosphorus and carbon. Following ageing, the samples were again fractured and analysed by AES.
It was found that increasing carbon bulk contents caused the grain boundary concentration of phosphorus to fall and the grain boundary concentration of carbon to increase. This result can be seen in Figure 5.5 for a Fe-0.17%P alloy. This effect between phosphorus and carbon has been termed site competition.

Site competition can be thought of in terms of atomic locations at the grain boundaries. There is a finite number of these locations, and therefore if two elements segregate to the grain boundary and attempt to occupy these locations, there will exist some degree of competition between the segregating elements to occupy the sites.

Figure 5.5: Variation of grain boundary concentration of phosphorus and carbon in Fe-0.17P aged at 600°C (from Erhart and Grabke[44])

Suzuki and co-workers[46] have also investigated the effect of carbon on the phosphorus segregation behaviour in alpha-iron. A master alloy, containing 0.52wt.% phosphorus and 0.022wt.% carbon was prepared. This alloy had trace impurities of sulphur, silicon, aluminium, manganese and oxygen. Samples were then taken from this material and annealed for a range of times in firstly wet, and then dry, hydrogen at 973K to decrease the carbon concentration within the alloy. The carbon concentrations obtained were 0.012, 0.008 and 0.002 wt.%. The samples were finally analysed using AES.

The results presented were interesting in that they appeared to contradict the site-competition effect, yet at the same time, also managed to agree with the effect. Their results showed that there was a positive correlation in each sample between phosphorus and carbon segregation. Thus, more carbon segregated to boundaries where more phosphorus segregated. However, examining the whole range of results obtained, it appeared that the average carbon segregation increases and the average phosphorus segregation decreases with increasing carbon bulk concentration. This latter point indicates that the site competition effect does occur.
However, the observation that more carbon segregated to boundaries where more phosphorus segregated was explained using a different effect. It was argued that there were two possible effects occurring; firstly, the segregation behaviour of both elements depends on the grain boundary structure, and secondly, there is some degree of co-segregation between the two elements.

The grain boundary structure will have a dramatic effect on the segregation behaviour, since the number of sites available for segregating atoms to locate at will vary from one boundary to the next. Therefore, if there exists a large number of available sites at the grain boundary, then both phosphorus and carbon will be able to segregate to the boundary, even though they are competing for the sites. Conversely, boundaries with a low number of available sites for atoms to locate at will correspondingly exhibit low segregation of both carbon and phosphorus.

The effect of co-segregation was also discussed. It was argued that if the segregation energy of carbon were greater than the sum of the phosphorus segregation energy plus the grain boundary binding energy between carbon and phosphorus, then the site competition effect would overshadow any co-segregation effect. Some of the results presented in this work are shown in Figure 5.6. They show that the degree of carbon segregation to grain boundaries decreases with increasing temperature and with increases with increasing bulk concentration. Phosphorus, on the other hand, exhibited a maximum level of segregation. This maximum level decreased with increasing carbon concentration.

![Figure 5.6: Experimentally observed segregation of Phosphorus and Carbon (from Suzuki and co-workers)](image)

The site competition between phosphorus and carbon has also been investigated by Hansel and Grabke. Their work examined two Fe-P-C alloys, with bulk phosphorus contents of 430wt.ppm and 1600wt.ppm. These alloys were then carbon-doped by placing the samples in a flowing $\text{CH}_4-\text{H}_2$ mixture at 700°C. The bulk carbon contents obtained ranged

74
from 10 to 100wt.ppm. The alloys were then subjected to differing annealing times and temperatures, ranging from 500°C to 700°C and from 1 day to 66 days. Following these ageing processes, the samples were analysed using AES.

The results they obtained for ageing temperatures of 550°C and 600°C are shown in Figure 5.7. The results show that there exists a maximum carbon grain boundary concentration. This concentration is determined by the carbon solubility limit at the two temperatures investigated, for 550°C this solubility limit is 30wt.ppm and for 600°C it is 60wt.ppm. For carbon contents above these solubility limits, the carbon becomes precipitated as cementite and taken out of solution. Once out of solution, the carbon has no further segregation effect. It was also found that the alloys containing higher carbon levels (above 60ppm), the samples did not fail inter-granularly. It was therefore difficult to obtain grain boundary compositions from these samples.

![Figure 5.7: Grain boundary concentrations of phosphorus and carbon versus carbon bulk content in a 1600wt.ppm phosphorus alloy aged at 550°C (from Hansel and Grabke[47])](image)

Thus far in the discussion, the site competition that exists between phosphorus and carbon has been highlighted. The discussion will now introduce some alternative interactions that have been investigated between phosphorus and other common alloying and impurity elements, for example, manganese, chromium, molybdenum and nitrogen.

The interactions between elements phosphorus, carbon, manganese and chromium were investigated by Weng and McMahon[48]. The compositions of the materials analysed in this work are shown in Table 5.2. A total of 10 alloy systems were analysed following ageing, using the technique of AES. Each alloy had a composition selected to highlight any interaction between the segregating elements.

It was found that increasing the carbon content of phosphorus-doped steel alloys caused the grain boundary concentration of phosphorus to fall, due to the site competition...
effect observed by Erhart and Grabke and discussed earlier in this section. However, the actual grain boundary concentration of carbon was unknown, since the concentration of carbon at the grain boundary was too low to be measured using the available equipment.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03%P</td>
<td>0.005</td>
<td>0.05</td>
<td>0.034</td>
<td>0.0023</td>
<td>&lt;0.10</td>
<td>0.0002</td>
</tr>
<tr>
<td>0.06%P</td>
<td>0.006</td>
<td>0.05</td>
<td>0.075</td>
<td>0.0009</td>
<td>&lt;0.10</td>
<td>0.0003</td>
</tr>
<tr>
<td>1%Mn</td>
<td>0.005</td>
<td>0.94</td>
<td>0.008</td>
<td>0.0014</td>
<td>0.02</td>
<td>0.0006</td>
</tr>
<tr>
<td>1%Cr</td>
<td>0.007</td>
<td>&lt;0.01</td>
<td>&lt;0.003</td>
<td>0.0021</td>
<td>1.00</td>
<td>0.0003</td>
</tr>
<tr>
<td>1Mn-0.03P</td>
<td>0.002</td>
<td>0.97</td>
<td>0.036</td>
<td>0.004</td>
<td>-</td>
<td>0.0009</td>
</tr>
<tr>
<td>2Mn-0.03P</td>
<td>0.002</td>
<td>1.89</td>
<td>0.036</td>
<td>0.006</td>
<td>-</td>
<td>0.0007</td>
</tr>
<tr>
<td>1Mn-0.06P</td>
<td>0.001</td>
<td>1.04</td>
<td>0.064</td>
<td>0.004</td>
<td>-</td>
<td>0.0007</td>
</tr>
<tr>
<td>1Cr-0.03P</td>
<td>0.003</td>
<td>-</td>
<td>0.034</td>
<td>0.005</td>
<td>1.04</td>
<td>0.0011</td>
</tr>
<tr>
<td>2Cr-0.03P</td>
<td>0.002</td>
<td>-</td>
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<td>0.005</td>
<td>2.06</td>
<td>0.0013</td>
</tr>
<tr>
<td>1Cr-0.06P</td>
<td>0.001</td>
<td>-</td>
<td>0.061</td>
<td>0.004</td>
<td>1.02</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

Table 5.2: Compositions of alloys (wt.%) analysed by Weng and McMahon[48]

This site competition effect demonstrated by Weng and McMahon was explained by the following argument. Carbon caused grain boundaries to become stronger, since lower carbon steels became brittle and fractured inter-granularly. Carbon forms covalent bonds with its surrounding iron atoms in a tetrahedral manner, causing the grain boundaries to more effectively bind together. This is the opposite effect of solute atoms, which bond by drawing charge from surrounding metal atoms, thereby weakening the metal-metal bonds. Thus, any site competition between phosphorus and carbon would cause the failure mode of the alloy to alter from brittle to ductile.

Sevc and co-workers[49-51] also performed work relating the segregation of phosphorus to the segregation of chromium, molybdenum, vanadium and carbon. The alloy system investigated was Fe-2.7Cr-0.7Mo-0.3V, with minor additions of carbon, manganese, silicon and sulphur. Three different alloys were produced, with phosphorus concentrations ranging from 0.004 to 0.027wt.%. The results obtained from their work are shown in Figure 5.8. The figure shows the relationship between the segregation of phosphorus and the elements chromium, molybdenum, vanadium and carbon. From the results they obtained, it was shown that there was a small molybdenum-phosphorus interaction energy, but this value was too low to significantly influence the segregation behaviour of phosphorus. The results also indicated that the segregation of both vanadium and molybdenum are higher for higher bulk phosphorus contents, indicating some form of interactive co-segregation effect. They also demonstrate that carbon segregation decreases for increasing phosphorus contents, indicating the site competition effect already introduced.
Figure 5.8: Correlation between the phosphorus grain boundary concentrations and the grain boundary concentrations of: (a) Cr, (b) Mo, (c) V and (d) C (from Sevc and co-workers[49])

Following the analysis of Fe-C-P alloys introduced earlier, Erhart and Grabke analysed the influence of Chromium on phosphorus and carbon segregation[44]. In a Fe-2.2Cr-0.048P alloy, aged at 500°C, it was found that the grain boundary concentration of P followed that exhibited by the Fe-P binary alloy. The grain boundary concentration of chromium was only slightly higher than the bulk concentration. This would indicate that there is little or no interaction between chromium and phosphorus.

However, it was found that adding carbon to the Fe-Cr-P alloy caused the grain boundary concentration of chromium to increase. The grain boundary phosphorus concentration in this alloy was also significantly higher than that found in the Fe-C-P alloy.
This would indicate that the addition of chromium to this system enhanced the grain boundary concentration of phosphorus. This 'interaction' could be explained by the formation of chromium carbides, which would take carbon out of solution and therefore reduce the carbon-phosphorus site-competition effect. The composition of this alloy, and the other alloys analysed, are shown in Table 5.3.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-P</td>
<td>0.001</td>
<td>0.016</td>
<td>0.046</td>
<td>0.004</td>
<td>0.05</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe-C-P</td>
<td>0.101</td>
<td>0.125</td>
<td>0.045</td>
<td>0.003</td>
<td>0.05</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe-Cr-P</td>
<td>0.001</td>
<td>0.033</td>
<td>0.048</td>
<td>0.003</td>
<td>2.20</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe-Cr-C-P</td>
<td>0.104</td>
<td>0.115</td>
<td>0.047</td>
<td>0.003</td>
<td>2.20</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 5.3: Alloy compositions analysed by Erhart and Grabke\textsuperscript{[44]}

Both Briant\textsuperscript{[52]} and Grabke and co-workers\textsuperscript{[53]} have investigated the effect of manganese on phosphorus diffusion and segregation. The work of Briant also examined the influence of nickel and chromium additions, which will be discussed in due course. The compositions of the materials examined by Briant are shown in Table 5.4. All of the samples were austenitized, followed by an oil quench, then tempered, followed by a water quench. The materials were then aged at 480°C for 500 hours, and then water quenched. Examination of the fractured samples was performed using AES. At least 20 boundaries from each alloy were analysed to obtain a representative average result.

The results indicated that there was no influence on phosphorus segregation behaviour by additions of manganese to the alloy. However, an argument was put forward that the additions of certain other elements caused the embrittling potency of the phosphorus to diminish, without having any affect on its segregation behaviour. This point will be discussed more when discussing the influence of chromium and nickel on the phosphorus segregation behaviour later in this section.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Ni</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.5</td>
<td>1.7</td>
<td>0.3</td>
<td>-</td>
<td>0.01</td>
<td>Bal.</td>
</tr>
<tr>
<td>B</td>
<td>3.5</td>
<td>1.7</td>
<td>0.3</td>
<td>-</td>
<td>0.03</td>
<td>Bal.</td>
</tr>
<tr>
<td>C</td>
<td>3.5</td>
<td>1.7</td>
<td>0.3</td>
<td>-</td>
<td>0.06</td>
<td>Bal.</td>
</tr>
<tr>
<td>D</td>
<td>4.6</td>
<td>2.8</td>
<td>0.3</td>
<td>-</td>
<td>0.06</td>
<td>Bal.</td>
</tr>
<tr>
<td>E</td>
<td>7.0</td>
<td>3.0</td>
<td>0.3</td>
<td>-</td>
<td>0.06</td>
<td>Bal.</td>
</tr>
<tr>
<td>F</td>
<td>5.9</td>
<td>2.0</td>
<td>0.3</td>
<td>-</td>
<td>0.10</td>
<td>Bal.</td>
</tr>
<tr>
<td>G</td>
<td>7.2</td>
<td>2.5</td>
<td>0.3</td>
<td>-</td>
<td>0.10</td>
<td>Bal.</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
<td>2.0</td>
<td>0.3</td>
<td>1.0</td>
<td>0.03</td>
<td>Bal.</td>
</tr>
<tr>
<td>I</td>
<td>3.6</td>
<td>2.0</td>
<td>0.3</td>
<td>1.0</td>
<td>0.04</td>
<td>Bal.</td>
</tr>
<tr>
<td>J</td>
<td>3.5</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>0.06</td>
<td>Bal.</td>
</tr>
<tr>
<td>K</td>
<td>3.5</td>
<td>4.5</td>
<td>0.3</td>
<td>-</td>
<td>0.06</td>
<td>Bal.</td>
</tr>
<tr>
<td>L</td>
<td>3.5</td>
<td>6.6</td>
<td>0.3</td>
<td>-</td>
<td>0.06</td>
<td>Bal.</td>
</tr>
<tr>
<td>M</td>
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<td>-</td>
<td>0.3</td>
<td>0.6</td>
<td>0.06</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 5.4: Compositions of alloys (wt.% ) analysed by Briant\textsuperscript{[52]}
Grabke and co-workers published work that investigated the sole effect on manganese on phosphorus segregation\textsuperscript{53}. The work examined two model alloys, firstly a Fe-Mn-0.05P system and secondly a Fe-Mn-0.15C-0.05P system. All samples were normalised and cooled, and then aged at 500°C for between 2 days and 4 weeks. The samples were then fractured and examined using AES.

The results of the grain boundary analyses were in agreement with those of Briant, in that there is no effect of manganese alone on phosphorus segregation. However, there did appear to be some enhancement of phosphorus segregation in the alloys with higher manganese contents. This was assumed to be due to interactions between manganese and carbon. It was shown that manganese decreases the carbon activity and solubility. Since carbon and phosphorus are in competition for available atom locations at grain boundaries, any decrease in the carbon concentration present within the material will therefore cause the grain boundary concentration of phosphorus to increase. The effect will therefore be in proportion to the manganese bulk concentration.

The manganese effect on the carbon solubility within the material is due to the formation of (Fe,Mn)$_3$C. This carbide has a lower solubility product than that of cementite, and will therefore be formed preferentially.

The work discussed earlier by Weng and McMahon\textsuperscript{48} also found that manganese segregated to grain boundaries. This would also lower the grain boundary cohesion, causing a more brittle material. However, it also appeared that manganese interacts with phosphorus during segregation processes. However, since many alloys contain amounts of carbon, which exhibits grain boundary site competition with phosphorus, any enhancement of phosphorus segregation due to manganese interactions would be negligible. The results indicated that a carbon concentration as low as 10-30ppm would have this effect. Although this negligible additional enrichment of phosphorus has little effect on the fracture strength of the material, the additional manganese at the boundary would cause a reduction in the fracture strength.

Moller, Brenner and Grabke\textsuperscript{54} investigated the effect of molybdenum on the segregation characteristics of phosphorus. Their analysis used the techniques of field ion microscopy and atom probe microanalysis to determine any possible interactions between Mo, P and C. The compositions of the alloys examined are shown in Table 5.5.

<table>
<thead>
<tr>
<th>Heat</th>
<th>Mo</th>
<th>P</th>
<th>Mn</th>
<th>C</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM1705</td>
<td>0.555</td>
<td>0.100</td>
<td>0.0360</td>
<td>-</td>
<td>99.310</td>
</tr>
<tr>
<td>SM1706</td>
<td>0.548</td>
<td>0.105</td>
<td>0.042</td>
<td>0.34</td>
<td>98.966</td>
</tr>
</tbody>
</table>

Table 5.5: Composition (at.\%) of materials analysed by Moller and co-workers\textsuperscript{54}

The results obtained indicated that molybdenum had no effect on the segregation of phosphorus in the C-free heat (SM1705). However, in the C-containing heat (SM1706), small Mo$_2$C precipitates were formed during ageing at 600°C for 17.5 hours. The size of these
precipitates was between 2 and 4 nm. During more prolonged ageing, larger precipitates grew, with diameters of up to 30 nm. Analysis of these precipitates showed that they contained no dissolved phosphorus.

Around these precipitates, there appeared to be some phosphorus enrichment. However, this phosphorus enrichment manifested itself in a region adjacent to the precipitate, although not exactly at the interface. This region extended up to 15 nm into the matrix, and had a concentration of 2 at.%, a figure considerably higher than the bulk concentration of the material. Although these results do not indicate any form of molybdenum-phosphorus interaction, they imply that the phosphorus may be trapped by the formation of molybdenum carbides. This trapping effect could be due to either the formation of dislocation structures adjacent to the precipitates, or by the precipitate being surrounded by a localised strain field.

Dumoulin and co-workers[55] analysed the effect of molybdenum in reducing the embrittlement of 2%Cr-1%Ni steels with variable molybdenum and phosphorus contents. A wide range of alloys were analysed, using Charpy impact toughness tests to highlight any change in the ductile-brittle transition temperature, and AES to examine the intergranular fracture surfaces. Any carbides that were found in the sample were also analysed, using carbon extraction replicas of the fracture surfaces and energy dispersive X-ray spectroscopy.

It was found that the addition of molybdenum to the alloys lowered their susceptibility to reversible temper embrittlement. However, in contrast to the results of Moller and co-workers, the segregation of molybdenum is enhanced by the presence of phosphorus, indicating some strong interaction between the two elements. The enhanced segregation of molybdenum appears to counteract the embrittling effect of the phosphorus present at the grain boundary. However, it was not known whether this effect was due to the molybdenum causing the cohesion of the grain boundary to improve. Additionally, the formation of molybdenum phosphides within the matrix of the material was demonstrated. This scavenging of phosphorus is by molybdenum is, however, very slow.

Molybdenum does have a strong affinity for carbon. This was demonstrated by the formation of carbides as either the ageing time, ageing temperature or molybdenum concentration increased. This factor would therefore be the limiting parameter in determining how beneficial molybdenum additions are to alleviating embrittlement.

Guillou and co-workers[56] have also examined the effect of molybdenum on the segregation of phosphorus, this time in 12%Cr martensitic stainless steel. Three alloys were analysed, each with different nominal molybdenum concentrations. These ranged from 0.1 to 0.98 wt.%. Samples of the alloys were then aged at 500, 550 and 600 °C, for periods ranging from 2 to 1000 hours. The samples were then fractured and analysed using AES to determine the grain boundary compositions. Argon sputtering was used to remove layers from the samples and to determine the depth of the segregated layers. This would also determine whether the Cr and Mo were segregated or precipitated.
The results were quite conclusive in demonstrating molybdenum does act as a remedy to reversible temper embrittlement, in agreement with the work of Dumoulin and co-workers. The results obtained are shown in Figure 5.9. The graphs show that as the nominal molybdenum content increases, both the intergranular phosphorus concentration and the ductile to brittle transition temperature fall.

![Figure 5.9: Influence of bulk molybdenum concentration on phosphorus segregation and on DBTT (from Guillou and co-workers)\(^{[56]}\)](image)

Increasing the molybdenum content caused the precipitation of molybdenum-rich carbides to be favoured. In addition, since molybdenum is a known ferrite stabiliser, high levels would have changed the microstructure from the martensitic structure being examined to a ferritic structure.

The effect of the chromium content of the alloys was also examined in relation to the segregation of both molybdenum and phosphorus. It was shown that Cr co-segregates with phosphorus. Since the segregation of Cr is typically low in these alloys, the presence of phosphorus within the alloy dramatically increased the Cr segregation.

Weng and McMahon\(^{[48]}\) also discussed the effect of chromium on the behaviour of steel alloys. It was found, in agreement with Erhart and Grabke\(^{[44]}\), that chromium is an effective scavenger of carbon. The results from alloys that were phosphorus-doped indicated that the addition of chromium caused the boundaries to become weakened. Since carbon and phosphorus are known to segregate competitively, any reduction in the grain boundary concentration of carbon, due for example to the formation of chromium carbides along the boundary, would cause the relative concentration of phosphorus to increase. This effect would have the outcome of causing the grain boundaries to become more brittle.
Results indicated also that phosphorus segregation was not enhanced by the presence of chromium, although the presence of phosphorus was thought to enhance the segregation of chromium, agreeing with the work of Guillou and co-workers. In addition, chromium itself causes weakening of grain boundaries, so this, coupled with phosphorus segregation, would cause severely embrittled boundaries.

Similar work performed by Suzuki highlighted the effects of chromium on phosphorus segregation\(^{[57]}\). In this work, alloys with essentially ternary compositions were prepared. These alloys had very small impurity concentrations so that the interactions between phosphorus and chromium could be more carefully monitored. A range of ageing times and temperatures were employed, and the samples were fractured and analysed using AES. The results obtained from the analyses indicated a lower interaction effect between the phosphorus and chromium than had been demonstrated by Guillou.

Briant\(^{[57]}\) discussed the effect of various elements on the grain boundary segregation of phosphorus in low alloy steels. The compositions of the materials tested have been shown in Table 5.4. The variations in the materials are the chromium, nickel, manganese and phosphorus concentrations.

The results obtained were very different compared to those of other workers. They showed that the degree of phosphorus segregation was independent of the levels of nickel, chromium and manganese in the alloy. The results indicated that the addition of these elements altered the embrittling potency of the phosphorus, which manifests itself by altering the fracture characteristics of the material. Whereas other workers made the assumption that if a sample would not fracture intergranularly, there was no segregated phosphorus at the grain boundaries, Briant suggested that there may well be phosphorus present, albeit in a less potent state. This suggestion is valid in light of the work investigating the interactions between phosphorus and molybdenum, which demonstrated that although the molybdenum did not lower the magnitude of phosphorus segregation, it did increase the coherency of the grain boundary. This in turn caused the fracture mode of the samples to change from brittle, intergranular failure to predominantly ductile failure. This was demonstrated by Briant by etching the samples with picric acid, which preferentially attacks grain boundaries that have phosphorus enrichment.

The observations of Briant are confirmed by the work of Grabke and co-workers\(^{[53]}\). This work set out purely to investigate the effect of manganese on the phosphorus behaviour in ferritic steels. They used alloys that were primarily Fe-Mn-P and Fe-Mn-C-P in their composition. The manganese contents vary from 0.5 to 9.4wt.%, so that the manganese effect on the phosphorus diffusion could be properly observed. The compositions of the alloys analysed are shown in Table 5.6.
Table 5.6: Compositions of alloys (wt.%) analysed by Grabke and co-workers[53]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mn</th>
<th>P</th>
<th>C</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.055</td>
<td>0.0028</td>
<td>0.0027</td>
<td>Bal.</td>
</tr>
<tr>
<td>2</td>
<td>2.01</td>
<td>0.055</td>
<td>0.0033</td>
<td>0.0029</td>
<td>Bal.</td>
</tr>
<tr>
<td>3</td>
<td>4.91</td>
<td>0.052</td>
<td>0.0029</td>
<td>0.0033</td>
<td>Bal.</td>
</tr>
<tr>
<td>4</td>
<td>9.39</td>
<td>0.051</td>
<td>0.0030</td>
<td>0.0039</td>
<td>Bal.</td>
</tr>
<tr>
<td>5</td>
<td>0.51</td>
<td>0.055</td>
<td>0.15</td>
<td>0.0027</td>
<td>Bal.</td>
</tr>
<tr>
<td>6</td>
<td>2.01</td>
<td>0.056</td>
<td>0.15</td>
<td>0.0030</td>
<td>Bal.</td>
</tr>
<tr>
<td>7</td>
<td>4.95</td>
<td>0.053</td>
<td>0.15</td>
<td>0.0035</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Samples of the alloys were normalised and then cooled to 500°C. They were then held at this temperature for between 2 days and 4 weeks to induce phosphorus segregation to grain boundaries. These samples were cooled to -120°C, and then fractured under vacuum, prior to being analysed using AES. Up to 10 grain boundaries from each sample were analysed in order to obtain a representative result.

The results showed that the grain boundary phosphorus concentration appears to be independent of the manganese content, indicating that there exists no preferential co-segregation interaction between the elements. The results also showed that manganese decreases the carbon activity and solubility. This causes a knock-on effect, since the carbon and phosphorus atoms compete for sites at grain boundaries. Thus, in alloys containing both manganese and carbon, the manganese reduces the carbon segregation, which then permits more phosphorus to locate at grain boundaries.

In addition, it was shown that manganese actively segregates to grain boundaries, and may also promote intergranular failure. Thus, alloys containing both phosphorus and manganese may exhibit more brittle fracture. Additional experimental work on the Fe-P and Fe-Mn-P alloys showed that manganese actually accelerates the diffusion of phosphorus. Therefore, the segregation of phosphorus in manganese containing alloys may be enhanced over a wide range of temperatures, causing embrittlement at lower temperatures than those typically associated with reversible temper embrittlement.

Nitrogen has also been shown to segregate to grain boundaries. The work of Erhart and Grabke[58] examined three alloys, each with different phosphorus and nitrogen levels. The levels of phosphorus in the alloys were 0.018, 0.064 and 0.33 wt.%. These alloys were then doped with nitrogen by holding them at 600°C and flowing NH₃-H₂ mixtures past them. This process leads to a well-defined nitrogen concentration in the materials. The samples were then placed in a UHV chamber and fractured at a pressure of 1.3x10⁻⁸ Pa and a temperature of -120°C, prior to analysis of the exposed fracture surfaces by AES.

In all samples, both nitrogen and phosphorus were found to have segregated to grain boundaries. Additionally, they found, by sputtering the samples and removing layers of atoms, that this segregation was localised to a few atomic layers on either side of the boundary, indicating a typical equilibrium segregation process.
The main findings, however, were that in samples with higher nitrogen contents, the grain boundary concentration of phosphorus was reduced, whereas the nitrogen grain boundary concentration increased. They noted also that by increasing the nitrogen concentration, the percentage of intergranular fracture that the sample exhibited decreased, indicating that the material has become less embrittled. This was attributed to the increased grain boundary cohesion that occurs when phosphorus is removed from the interface.

In addition to the segregation of phosphorus in iron-base alloys during isothermal ageing processes, there has also been work performed investigating the behaviour of other impurity elements. Sulphur is known to cause embrittlement of grain boundaries in iron alloys at both low and high temperatures. Suzuki and co-workers\(^{[59]}\) performed work on a series of alloys to investigate if there exists any competition between carbon and sulphur, in a similar manner to the competition that has been shown to exist between carbon and phosphorus. A range of alloys with compositions of between 8 and 100 wt.ppm of sulphur and between 12 and 90 wt.ppm carbon were prepared and aged at a range of temperatures. The samples were analysed using AES.

Their results indicated that there does indeed exist a site competition effect between carbon and sulphur for grain boundary sites in α-iron. They also demonstrated that for a given grain boundary concentration, sulphur is more embrittling than phosphorus. Their results indicated that the ductile to brittle transition temperature increased by 40K per 1 at.% increase in grain boundary concentration of sulphur, whereas phosphorus only caused an increase of 20K.

McMahon and co-workers performed experimental work examining the effects of antimony on a low-carbon Ni-Cr steel\(^{[60]}\). Since antimony is an element from Group V of the periodic table (see Table 5.1), it can be expected to be a highly segregating element. This will cause the grain boundary energy to fall and therefore to lower the cohesion of the boundary. Their findings indicated that there was a clear correlation between the segregation between antimony and nickel. Also, in Fe-C-Sb alloys there is no apparent segregation of antimony whereas in Fe-Ni-Cr-C-Sb alloys with the same bulk content of antimony there is definite antimony segregation. Additionally, they found that these results correlated well to changes in the ductile to brittle transition temperature, as shown in Figure 5.10 for samples aged at 520°C.

In addition to the work discussed earlier, Briant has examined the segregation and co-segregation behaviour of antimony and nickel in iron\(^{[61,62]}\). The results show that increases in the bulk content of antimony cause the magnitude of the segregated antimony to increase. Additionally, the results indicated that increases in the bulk content of nickel caused a corresponding increase in the segregated antimony at the grain boundaries. However, they found that manganese additions reduced the segregation of antimony by forming nickel-manganese antimonides. The authors dispute the theory of co-segregation in explaining their results. Instead, they state that the dominant mechanism in governing the segregation
behaviour of antimony is the effect of the other alloying additions on the solubility of antimony. Briant also investigated the influence of nickel segregation on the behaviour of phosphorus in low-alloy steels. However, there appeared to be no nickel influence from the results obtained.

![Graph showing transition temperature and intergranular fracture percentage with ageing time at 520°C.](image)

**Figure 5.10:** (a) Increase in transition temperature, and percent intergranular fracture with time of ageing at 520°C; (b) Corresponding increase in the grain boundary concentrations of antimony and nickel.

### 5.2.2 Theoretical modelling of TES

The discussion presented in the Section 5.2.1 highlighted the wide range of experimental work that has been published surrounding the subject of thermal equilibrium segregation of phosphorus and other alloying and impurity elements within steel alloys. This section will introduce the theoretical work that has been published, starting with the simple case of predicting the behaviour of one impurity element in a binary alloy. Following this, the discussion will progress onto the wider ranging work that has been performed to model the effects of interactive co-segregation, and grain boundary site competition between elements within a ternary alloy system.
5.2.2.1 Modelling TES in binary alloys

The basic equation for predicting the thermal equilibrium segregation of a non-metallic impurity element, $I$, to the grain boundary of iron was determined by McLean\textsuperscript{[63]} from the original statistical thermodynamics of Gibbs. Gibbs calculated that elements that lower the surface energy of a system will become enriched at the surface. The phenomenon is therefore sometimes referred to as Gibbsian segregation. McLean took the statistical mechanics concept of the division of solute or impurity atoms between two states of different free energy, i.e. the grain boundary and the matrix. This was then analogised with the Langmuir gas adsorption isotherm. This assumed that there is a single layer, a single adsorbate (segregant), a fixed number of sites at which the adsorbate can locate, and that no site-to-site interaction exists. The Langmuir-McLean isotherm can be expressed as:

\[
\frac{X_f}{X^{0\phi} - X_f} = \frac{X_i}{1 - X_i} \exp\left(\frac{\Delta G_i}{RT}\right)
\]

where:
- $X_f$ is the concentration of $I$ at equilibrium (infinite time) at the grain boundary, $\phi$.
- $X_i$ is the concentration of $I$ dissolved in the matrix.
- $X^{0\phi}$ is the total ratio of all the sites available at the interface for segregation.
- $\Delta G_i$ is the segregation free energy of the particular non-metallic impurity element being considered (also expressed as $\Delta G_i^0$), determined from $\Delta G_i = \Delta H_i^0 - T \Delta S_i^0$.
- $\Delta H_i^0$ is the standard molar enthalpy of segregation in a dilute binary alloy.
- $\Delta S_i^0$ is the standard molar entropy of segregation in a dilute binary alloy.
- $R$ is the gas constant.
- $T$ is the absolute temperature.

From this equation, it is obvious that the predicted segregation rises as solute content rises, or as the temperature falls. In addition, owing to the fixed number of sites available at the interface for segregating elements to locate at, the segregation will eventually reach saturation, i.e. equilibrium concentration. A more commonly used version of this equation is:

\[
C_b = \frac{\beta C_g \exp\left(\frac{Q}{kT}\right)}{1 - \beta C_g \exp\left(\frac{Q}{kT}\right)}
\]

where:
- $C_b$ is the grain boundary concentration of solute.
- $\beta$ is a constant related to the grain boundary vibrational entropy, equal to 0.775.
- $C_g$ is the bulk concentration of the segregating solute element.
- $Q$ is the solute atom binding energy.
- $k$ is Boltzmann’s constant.
Figures 5.11 and 5.12 show the relationship between grain boundary concentration at equilibrium (infinite) time and temperature for a range of segregation energies. The concentration range in each of the two graphs extends to a value of unity. This concentration is termed monolayer coverage. Assuming that one third of the sites are expanded, one third are compressed and the remaining third are un-altered, monolayer coverage is approximately 30 atomic percent. Taking the boundary to be 3 atomic layers thick, unit concentration is equivalent to the number of solute atoms that are required to form a mono-molecular layer at the grain boundary.

Figure 5.11: Relationship between grain boundary concentration and temperature (bulk concentration = 1at.%, Q has units of cal/mol) (from McLean [63])

Figure 5.12: Relationship between grain boundary concentration and temperature (bulk concentration = 0.01at.%, Q has units of cal/mol) (from McLean [63])

\[1\] To convert cal/mol into eV/atom, divide by 23045
These equations, however, take no account of the time necessary for the diffusion of the impurity atoms to the grain boundaries. Recalling the discussion of the experimental work, very long ageing times were employed in order to ensure that equilibrium had been reached. In those pieces of work where a range of ageing times were used, it was shown that the time period is critical in the segregation behaviour of solute atoms. This kinetic improvement to the equation above was determined by McLean using diffusional analysis\textsuperscript{[63]}. McLean applied Ficks laws for diffusion from two semi-infinite half crystals, taking into account a constant enrichment factor. The resulting equation becomes:

\[
\frac{C_b(t) - C_g}{C_b - C_g} = 1 - \exp \left( \frac{4D_t t}{\alpha^2 d^2} \right) \text{erfc} \left( \frac{4D_t t}{\alpha^2 d^2} \right)^{1/2}
\]  

(5.3)

where:  
- $C_{b0}$ is the grain boundary concentration at time $t$.  
- $\alpha$ is equal to $C_{b0}/C_g$  
- $D_i$ is the diffusion coefficient of the impurity in the matrix.  
- $d$ is the grain boundary width.

By analysing the above kinetic expression, it is possible to derive times to reach certain concentrations at the grain boundary. Thus, the time taken to reach half monolayer coverage can be calculated from\textsuperscript{[41]}:

\[
t = \frac{0.591 \alpha^2 d^2}{4D_i}
\]

(5.4)

In addition, times to reach alternative fractions of monolayer coverage have been presented in the literature\textsuperscript{[41]}.

### 5.2.2.2 Determination of diffusion coefficients

The equation presented for kinetically predicting the equilibrium segregation (Equation 5.3) requires knowledge of the diffusivity of the segregating element. The diffusivity of phosphorus has been determined by a number of workers, both in isolation\textsuperscript{[44,64]} and when co-segregating with other elements, which will be discussed later. Indeed, many of these workers have used curve-fitting techniques to their experimentally observed segregation results to determine these values. The diffusivities of elements are typically expressed in the available literature using an Arrhenius-type expression:

\[
D_i = D_{0,i} \exp \left( \frac{-E_i}{kT} \right)
\]

(5.5)

where:  
- $D_{0,i}$ is the pre-exponential constant of the element diffusivity.  
- $E_i$ is the activation energy of the element, in units of eV per atom\textsuperscript{2}.

\textsuperscript{2} Many authors present diffusion activation energies in terms of kJ/mol. To convert kJ/mol into eV/atom, divide by 96.486
Mackenbrock and Grabke[45] determined the diffusivity of phosphorus in 12Cr-1Mo-V steel using the technique of radioactive tracer. The method used was to deposit a layer of radioactive phosphorus-32 on one surface of a 12mm diameter, 4mm thick, disc-shaped sample. Following a range of annealing processes, with temperatures between 703 and 752°C and times between 264 and 1440 hours, the penetration of the radioactive tracer was measured using the method of residual activity. This method removes layers from the surface of the sample. The thickness and mass of the layers is measured, and the radioactivity is recorded. From their results, the bulk and grain boundary diffusivities of phosphorus were determined. They were quoted as:

\[
D_{\text{bulk}} = 93.89 \exp \left( \frac{-405.3 \text{kJmol}^{-1}}{RT} \right) \text{m}^2\text{s}^{-1}
\]

\[
D_{\text{gb}} = 13.75 \times 10^4 \exp \left( \frac{-321.7 \text{kJmol}^{-1}}{RT} \right) \text{m}^2\text{s}^{-1}
\]

It can be seen from these figures that phosphorus can segregate far more rapidly along grain boundaries than it can through the matrix material. This behaviour should be born in mind when discussing precipitation in Chapter 7.

As a means of comparison, the value of the diffusivity of phosphorus was obtained by Mackenbrock and Grabke from curve fitting the experimentally observed segregation results. The figure obtained using this approach was:

\[
D = 3.32 \times 10^{-4} \exp \left( \frac{-273 \text{kJmol}^{-1}}{RT} \right) \text{m}^2\text{s}^{-1}
\]

Comparison of the figures indicates that the phosphorus segregation behaviour appeared to be determined by the diffusion of phosphorus along fast diffusion paths, instead of by bulk diffusion. These fast diffusion paths include the dislocation network present in the system, together with other microstructural features such as low-angle grain boundaries. These, in turn, feed the high angle boundaries with phosphorus. Again, this observation highlights the importance of considering the microstructure of the material when modelling segregation behaviour.

The diffusivities of phosphorus in the matrix material and along grain boundaries have also been predicted by Militzer and Wieting[65]. The diffusivities and activation energies obtained for a range of temperatures are shown in Table 5.7. It was assumed that the pre-exponential constant for both bulk and grain boundary diffusivities was 1.65x10^-4 m^2s^-1, which is the figure obtained for the diffusion of phosphorus in pure iron. These figures are somewhat different to those published by Mackenbrock and Grabke. The difference in the figures was attributed to the effects of ferromagnetism in the material.
Table 5.7: Pre-exponential constants and activation energies for the bulk and grain boundary diffusion of phosphorus at different temperatures (from Militzer and Wieting[65])

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>703</th>
<th>728</th>
<th>752</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_b$ (m²s⁻¹)</td>
<td>$2.2 \times 10^{-20}$</td>
<td>$7.2 \times 10^{-19}$</td>
<td>$2.9 \times 10^{-19}$</td>
</tr>
<tr>
<td>$D_{gb}$ (m²s⁻¹)</td>
<td>$8.8 \times 10^{-13}$</td>
<td>$2.0 \times 10^{-12}$</td>
<td>$6.1 \times 10^{-12}$</td>
</tr>
<tr>
<td>$Q_b$ (eV)</td>
<td>3.07</td>
<td>3.05</td>
<td>3.00</td>
</tr>
<tr>
<td>$Q_{gb}$ (eV)</td>
<td>1.60</td>
<td>1.54</td>
<td>1.51</td>
</tr>
</tbody>
</table>

5.2.2.3 Theoretical Modelling of ternary TES

The theoretical modelling of ternary alloys has been performed most successfully by Guttmann and co-workers[42,66-68]. In the Guttmann model, the basic equations that are used are very similar to those used for modelling binary alloy systems. However, in order to model ternary systems, it is necessary to distinguish between alloys where there exists only one type of site at the grain boundary and alloys where there are independent sites at the grain boundary. These scenarios can be more easily described as site competition and non-competitive co-segregation.

**Non competitive co-segregation theory**

The approach adopted for modelling the non-competitive co-segregation of a non-metallic impurity element (I) and a transition metal element (M) assumes that at the grain boundary there exists two independent sites, or sub-lattices, at which the elements can occupy. These sites have fractions $c'$ and $a'$ existing at the boundary, where $c'+a'=1$. The equation governing the segregation behaviour of the segregating elements is:

$$
\frac{Y^d_i}{1 - Y^d_i} = X^b_i \exp \left( \frac{\Delta G_i}{RT} \right) \quad \text{for } i=I,M
$$

(5.6)

where: $Y^d_i$ are the concentrations of I and M in their sub-lattices at the boundary.

$$
\Delta G_i = \Delta G^0 + \frac{\beta}{c'} Y^d_M
$$

$$
\Delta G_M = \Delta G^0 + \frac{\beta}{a'} Y^d_I
$$

$\beta$ is the preferential M-I interaction coefficient.

This equation is essentially the same as that of the binary model, but with modifications to the equilibrium segregation energy of each segregating element due to the M-I interaction. This interaction between the two elements governs the overall behaviour of the segregation behaviour. Metallic elements, which are strongly attracted to highly segregating impurity elements, will also segregate, and may even enhance the segregation of the impurity element. However, if there is little or no interaction between the elements, then
the impurity element’s segregation behaviour will be unaltered. However, exceptionally high interaction coefficients may promote the formation of stable compounds.

**Site competition theory**

This theory takes into consideration the interactions between the non-metallic impurity elements (I) and the transition metal elements (M). It assumes that there is only one type of lattice site at the grain boundary. The two segregating elements are therefore in competition to occupy these locations. The segregating elements therefore compete to occupy these grain boundary lattice sites. Thus, the segregating impurity element, for example phosphorus, would at maximum reach levels of segregation predicted by the equation presented for binary systems, since it cannot occupy more than 100% of the available lattice sites. Therefore, any competing element that segregates strongly on the same lattice sites will cause a significant drop in the predicted segregation of the impurity element. The equation can be expressed thus:

\[
\frac{X_I^f}{1 - X_I^f - X_M^f} = X_I^s \exp \left( \frac{\Delta G_I}{RT} \right) \text{ for } i=I,M
\]

where:

\[\Delta G_I = \Delta G_I^0 + \alpha' X_M^f\]

\[\Delta G_M = \Delta G_M^0 + \alpha' X_I^f\]

\[\alpha' \text{ is a constant for the preferential interaction between M and I at the boundary.}\]

The equation presented here has been extended to model irradiation enhanced ternary equilibrium segregation, incorporating site competition effects during the service life of the reactor. This will be discussed in Chapter 6 which discusses radiation induced segregation, since the diffusion parameters of the segregating elements will need to be modified due to the effects of irradiation.

**Kinetic modelling of ternary TES**

The modelling approach developed by McLean for predicting equilibrium segregation in binary alloy systems incorporated a kinetic appraisal of the process. However, incorporating a kinetic effect into the two models of ternary segregation requires a number of assumptions to be made. Consider the case of two elements, A and B, segregating to a grain boundary containing only one sub-lattice; the site competition model. Element A may segregate to the boundary more rapidly than the element B. However, the element B may well have a higher segregation enthalpy than element A, and would therefore displace the element from the boundary. Thus, at short times, there may be a higher grain boundary concentration of element A, but after longer periods, element B will begin to remove element A from the boundary.
A theoretical appraisal of the kinetics of ternary ES has been performed by Militzer and Wieting\textsuperscript{[69]}. This approach considered the segregation of elements due to both isothermal-ageing conditions, and to cooling processes. The model therefore could also be categorised as a non-equilibrium segregation model, which are discussed in the following section of this Chapter. Although the derivation of the model is somewhat complex, the final equation for predicting the segregation can be expressed as:
\[
C_i(t) = C_i(0) + 2 \left( \frac{C_i^0}{\sqrt{\pi} \delta} \right) \sqrt{\int D_i(t') dt'} - \frac{1}{\sqrt{\pi} \delta} \int C_i(t') D_i(t) dt'
\]  
(5.8)

where: 
- $C_i(t)$ is the grain boundary concentration of element $i$ at time $t$. 
- $C_i(0)$ is the grain boundary concentration of element $i$ at time $0$. 
- $C_i^0$ is the bulk concentration of element $i$.

However, the ternary model used in this Thesis uses a modified version of the kinetic equation for binary equilibrium segregation. This equation was presented earlier as Equation 5.3. The modification to this equation assumes that the maximum value of the grain boundary concentration, $C_b$, is obtained from the particular ternary equilibrium segregation equations (Equation 5.6 or 5.7). Thus, the grain boundary concentration at any time, $C_b(t)$, can be determined for each element.

5.2.2.4 Determination of diffusivities and interaction coefficients

In Section 5.2.1.2, a range of experimentally-observed segregation results were discussed. In most cases, these same pieces of work went on to compare the experimental observations with predictions that the various theoretical models gave. Where necessary, improved theoretical parameters for the diffusion of the segregating elements were presented, and some of these will be summarised in this brief section.

The free energies of phosphorus and carbon segregation have also determined from analysis of experimental results by Hansel and Grabke\textsuperscript{[47]}. The figures obtained were:
\[
\Delta G_P^0 = -21200 + 37.3T \text{ J/mol}
\]
\[
\Delta G_C^0 = -37700 - 43.2T \text{ J/mol}
\]

From Erhart and Grabke\textsuperscript{[44]}, the free energy of carbon segregation was determined at 600°C from analysis of results obtained from AES experiments. The figure quoted was
\[
\Delta G_C^0 = -76 \text{kJ/mol},
\]
which corresponds well to the $-75.4 \text{kJ/mol}$ that the relationship of Hansel and Grabke predicts. Suzuki and co-workers\textsuperscript{[46]} also presented calculations for the segregation free energies of both phosphorus and carbon. The figures presented were 50kJ/mol and 80kJ/mol, respectively.
The effect of manganese on the bulk and grain boundary diffusion of phosphorus has been investigated by Grabke and co-workers[53]. The bulk phosphorus diffusivities in Fe-P and Fe-2Mn-P alloys were expressed as:

\[ D_{Fe-P} = 9.55 \times 10^{-6} \exp\left(\frac{-212\text{kJmol}^{-1}}{RT}\right) \text{m}^2\text{s}^{-1} \]

\[ D_{Fe-2Mn-P} = 1.43 \times 10^{-4} \exp\left(\frac{-227\text{kJmol}^{-1}}{RT}\right) \text{m}^2\text{s}^{-1} \]

These results indicate that the diffusion of phosphorus is enhanced by additions of manganese, in agreement with the calculations of Seah[64]. Likewise, the grain boundary diffusivities of phosphorus are expressed as:

\[ D_{Fe-P} = 5.59 \times 10^{-11} \exp\left(\frac{-175\text{kJmol}^{-1}}{RT}\right) \text{m}^3\text{s}^{-1} \]

\[ D_{Fe-2Mn-P} = 4.05 \times 10^{-12} \exp\left(\frac{-149\text{kJmol}^{-1}}{RT}\right) \text{m}^3\text{s}^{-1} \]

The segregation free energies of phosphorus and chromium and their interaction energies were calculated by Guillou[56]:

\[ \Delta G^0_P = 46\text{kJmol}^{-1} \]

\[ \Delta G^0_C \approx 0\text{kJmol}^{-1} \]

\[ \beta^b_{Cr-P} = 17.1 \pm 2.4\text{kJmol}^{-1} \]

These figures indicate that chromium alone has a low driving force for segregating to grain boundaries, and that and additions of phosphorus will increase its segregation. Owing to the low chromium content of the alloys considered in this Thesis, no predictions of chromium segregation will be presented. These figures, however, are useful for comparison with the data that will be used for the manganese and molybdenum predictions later.

### 5.3 Thermal non-equilibrium segregation

In the previous section, the phenomenon of equilibrium segregation was introduced, and theoretical models that predict the effect were discussed. From the discussion, it is obvious that the phenomenon occurs at constant temperature, i.e. during an isothermal ageing process that a material may undergo during a heat treatment process, or during service. Since the original theories for equilibrium segregation were developed by Gibbs, McLean and more recently Guttmann, researchers have become more interested in what occurs to material when temperatures are changing rapidly, such as during a quench. During quenching, important microstructural changes to materials can occur. When quenched, the material is under non-equilibrium conditions, since the material cannot respond to the temperature change in order to return to equilibrium conditions. Thus, the mechanism of
segregation that produces equilibrium segregation cannot occur. Therefore, a different mechanism produces the type of segregation observed. This is now generally known as thermal non-equilibrium segregation (TNES). The following sections will present and discuss the various experimental results that have been presented in the literature, and discuss the two non-equilibrium segregation theories that are used.

5.3.1 Experimental observations of TNES

Although the aim of this review is to discuss the segregation behaviour of phosphorus in ferritic steels, it is necessary in some places to discuss the segregation of other elements in different matrices. The first observation of TNES was by Westbrook[70] who observed that the hardness of grain boundaries increased in a range of quenched materials. Since the theory for TES could not explain the phenomena, it was suggested that an alternative mechanism of segregation was occurring. This process is the process which is now termed TNES.

Possibly the most significant piece of work in this area was performed by Karlsson, Norden and Odelius[71-74]. The work investigated the non-equilibrium segregation of boron in austenitic stainless steel. The methods used to determine the segregation were secondary ion mass spectrometry (SIMS), TEM, field ion microscopy, atom probe and imaging atom probe (IAP). These techniques, some of which have been discussed in Chapter 3, are of great use in examining very fine scale microstructural phenomena. The techniques of STEM-EDS and electron probe microanalysis (EPMA) were not used to analyse grain boundary segregation, owing to their low sensitivity for detecting boron.

The materials examined were low boron AISI 316L, high boron AISI 316L and Mo-free AISI 316L stainless steels. The low boron material contained less than 1ppm boron; the high boron contained 40ppm boron, and the Mo-free contained 23ppm boron. The compositions of these three alloys can be seen in Table 5.8. These materials were subjected to a range of heat treatments. The ageing temperatures varied between 900°C, 1075°C and 1250°C. The cooling rates varied between water quenching (approximately 530°C/s), cooling in a stream of cold argon gas (approximately 30°C/s) and air cooling (approximately 0.3°C/s). In all, 20 different conditions were analysed.

<table>
<thead>
<tr>
<th>Al</th>
<th>B</th>
<th>C</th>
<th>Cr</th>
<th>Co</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low B</td>
<td>0.03</td>
<td>&lt;1ppm</td>
<td>0.015</td>
<td>17.4</td>
<td>0.02</td>
<td>0.03</td>
<td>bal.</td>
<td>1.76</td>
<td>2.61</td>
<td>0.05</td>
<td>13.1</td>
<td>0.01</td>
<td>3ppm</td>
<td>0.01</td>
</tr>
<tr>
<td>High B</td>
<td>0.03</td>
<td>40ppm</td>
<td>0.016</td>
<td>17.5</td>
<td>0.02</td>
<td>0.04</td>
<td>bal.</td>
<td>1.76</td>
<td>2.62</td>
<td>0.05</td>
<td>13.2</td>
<td>0.01</td>
<td>3ppm</td>
<td>0.01</td>
</tr>
<tr>
<td>Mo-free</td>
<td>0.02</td>
<td>23ppm</td>
<td>0.016</td>
<td>17.4</td>
<td>0.02</td>
<td>0.01</td>
<td>bal.</td>
<td>1.80</td>
<td>0.01</td>
<td>0.04</td>
<td>13.2</td>
<td>0.01</td>
<td>2ppm</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 5.8: Composition (wt.%) of the alloys examined by Karlsson and co-workers[71]

The first paper of the series[71] examined the large-scale segregation behaviour of boron, using the analytical technique of SIMS. The technique of SIMS rasters an ion probe
over the surface of the specimen and records the emission of negatively charged secondary ions. This signal can be used to determine a mass-resolved ion image. The details of the technique used for these analyses were an ion probe of 14.5keV O$_2^+$ions, with a probe current of 2μA and a diameter of 100μm. The surface area analysed was 200 by 200μm.

The results indicated that boron became enriched at grain boundaries, steps on twin boundaries, in precipitates as well as at some unidentified regions within the matrix of the material. In the high-boron steel, it was found that the degree of boron segregation increased with increasing starting temperature and decreasing cooling rate. Similar findings were observed for both the Mo-free steel and the low-boron steel.

The second paper in the series concentrated on the finer scale segregation behaviour of boron, and aimed to quantify the magnitude of the segregation. Whereas the first paper used SIMS to detect segregation, this work used the techniques of TEM, FIM, AP and IAP. These techniques have all been discussed in some detail in Chapter 3. The results obtained from these analyses showed that the width of the boron enriched zone around the boundaries investigated increased with increasing starting temperature and lower cooling rates. However, they found that the amount of segregated boron increased with increasing starting temperature, but was highest for materials that were cooled at intermediate cooling rates, typically 13°C/s.

Several papers have been written discussing the non-equilibrium segregation behaviour of various elements in 2%Cr-1Mo steel, which is a commonly used steel in the electrical power generating industry[75-77]. These papers are of interest in a variety of ways. Firstly, they have been written over a period of 12 years, and as such highlight the various improvements that have been made, both in terms of the quality of experimental work, as well as in theoretical modelling. Secondly, they serve as a useful comparison to the material under investigation in this thesis, since both materials are intended for similar applications in the power generating industries.

The first paper in the series was written in 1981 by Doig and Flewitt[71]. The work examined 2%Cr1Mo steels in various conditions using an early STEM-EDS system, and compared the observed results to predictions obtained from a theoretical model. The details of the model will be discussed in the following section.

The material was prepared in the form of short rods, 25mm in length and 4mm in diameter. These rods were austenitised at 1423K and 1323K, and then quenched into water. The austenitisation process took 7.2x10$^3$ seconds (2 hours). Thin discs were then machined from the rods and suitably prepared for examination.

The STEM system was estimated to have an incident probe size of around 5nm, which compared to today’s current FEGSTEM probe sizes of around 1nm can be considered quite large. However, at the time, this was considered quite satisfactory in order to be able to detect segregation of various elements in regions around grain boundaries. Point analyses were performed on prior-austenite grain boundaries, and then at regions up to 150nm from
the boundary. The results indicated that the segregated layer adjacent to the grain boundaries was less than 20nm wide. It was also found that the only element segregating during the two quenching processes was chromium. Grain boundary concentrations of up to 12% were recorded, corresponding to enrichments of the order of 5 times the bulk content.

Further work by Doig and Flewitt\textsuperscript{[76]} investigated the segregation behaviour of both chromium and tin in 2\%Cr1Mo and 2\%Cr1Mo0.08Sn ferritic steels, and in AISI Type 316 austenitic stainless steel, again using the analytical technique of STEM-EDS. The ferritic samples were austenitized at 1423K, 1323K and 1223K for 2 hours before quenching into water. The AISI Type 316 austenitic stainless steel samples were heat treated at the same temperatures before being slowly cooled in argon gas, at a rate of approximately 0.025°C/s.

The microanalysis technique used was a STEM fitted with a tungsten filament, giving an incident electron probe size of approximately 8nm. This meant that any results obtained would be averaged over this area and would not be truly representative of the actual concentration at the centre of the area of interest. Point analyses were performed directly on the grain boundary, together with positions along a line perpendicular to the boundary up to 500nm into the grain.

The results indicated that chromium was the only segregating species in the 2\%Cr1Mo steel, and that tin was the only segregating species in the 2\%Cr1Mo0.08Sn steel. The actual results obtained from the STEM-EDS equipment can be seen in Table 5.9. As with the material analysed in the previous work, the enrichments of the segregating species are localised to within a few nanometres of the grain boundary. Likewise, owing to the finite size of the electron beam probe, the grain boundary concentration is only going to be a fraction of the actual concentration of the elements on the grain boundary.

<table>
<thead>
<tr>
<th>Alloy (Element)</th>
<th>Temp (K)</th>
<th>Position (nm)</th>
<th>Gb</th>
<th>20nm</th>
<th>50nm</th>
<th>100nm</th>
<th>200nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Cr1Mo (chromium)</td>
<td>1423</td>
<td>3.23</td>
<td>2.10</td>
<td>2.01</td>
<td>2.00</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>1323</td>
<td>2.54</td>
<td>2.09</td>
<td>2.11</td>
<td>2.23</td>
<td>2.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1223</td>
<td>2.17</td>
<td>1.95</td>
<td>2.02</td>
<td>2.08</td>
<td>2.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2%Cr1Mo0.08Sn (tin)</td>
<td>1423</td>
<td>3.81</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1323</td>
<td>1.30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1223</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.9: EDS results for Cr and Sn segregation (from Doig and Flewitt\textsuperscript{[76]})

More recently, Vorlicek and Flewitt\textsuperscript{[77]} examined the non-equilibrium segregation of phosphorus and tin in heats of 2\%Cr1Mo steel and submerged arc weld metal using FEGSTEM microanalysis. Compared to the techniques used in the previous two papers, this technique offers far better spatial resolution owing to the use of the field emission gun electron source in the microscope. The materials, whose compositions are shown in Table 5.10, were austenitized for 2 hours prior to cooling. The 2\%Cr1Mo steel samples were cooled at three different rates, from 1323K, which is approximately 0.7 of the absolute
melting temperature of the material, to room temperature. The cooling processes used were water quenching, air-cooling and furnace cooling.

The submerged arc weld material was cut from a Magnox RPV during construction. This material was subjected to a heat treatment that consisted of heating at approximately 20°C per hour to 923K, where it was held for 4 hours, prior to being cooled to 473K at 10°C per hour. This process was supposed to simulate the stress relief heat-treatment undertaken on the reactor pressure vessel during construction in 1962.

<table>
<thead>
<tr>
<th>Element</th>
<th>C (wt%)</th>
<th>Mn (wt%)</th>
<th>S (wt%)</th>
<th>P (wt%)</th>
<th>Si (wt%)</th>
<th>Cr (wt%)</th>
<th>Ni (wt%)</th>
<th>Mo (wt%)</th>
<th>Sn (wt%)</th>
<th>As (wt%)</th>
<th>Sb (wt%)</th>
<th>Cu (wt%)</th>
<th>Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2½Cr1Mo-Sn</td>
<td>0.081</td>
<td>0.46</td>
<td>0.007</td>
<td>0.28</td>
<td>2.27</td>
<td>0.15</td>
<td>1.00</td>
<td>0.077</td>
<td>0.006</td>
<td>0.020</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2½Cr-1Mo-P</td>
<td>0.086</td>
<td>0.46</td>
<td>0.009</td>
<td>0.29</td>
<td>0.28</td>
<td>0.15</td>
<td>1.00</td>
<td>0.011</td>
<td>0.005</td>
<td>0.021</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weld metal</td>
<td>0.092</td>
<td>1.52</td>
<td>0.035</td>
<td>0.29</td>
<td>0.48</td>
<td>0.05</td>
<td>0.09</td>
<td>0.01</td>
<td>0.04</td>
<td>0.003</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.10: Chemical composition of 2½Cr1Mo steel and weld metal analysed by Vorlicek and Flewitt [77]

The results indicated that in the higher phosphorus material there was segregation to prior austenite grain boundaries of P, Cr, Mn and Mo for all three cooling rates. The figures obtained from these experiments are shown in Table 5.11(a). The higher tin material did not exhibit tin segregation in the water-quenched condition, but did in both of the other samples. In agreement with the results presented previously, the width of the segregated region adjacent to the grain boundaries was observed to be around 20nm.

<table>
<thead>
<tr>
<th>Element</th>
<th>Water Quenched</th>
<th>Air Cooled</th>
<th>Furnace Cooled</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;150&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>C&lt;sub&gt;150&lt;/sub&gt;</td>
</tr>
<tr>
<td>2½Cr1Mo-P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.10</td>
<td>1.36</td>
<td>0.25</td>
</tr>
<tr>
<td>Cr</td>
<td>2.46</td>
<td>3.10</td>
<td>2.49</td>
</tr>
<tr>
<td>Ni</td>
<td>0.29</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>Mo</td>
<td>2.50</td>
<td>5.55</td>
<td>1.84</td>
</tr>
<tr>
<td>Mn</td>
<td>0.39</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>2½Cr1Mo-Sn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>0</td>
<td>0.02</td>
<td>0.14</td>
</tr>
<tr>
<td>Cr</td>
<td>2.72</td>
<td>3.96</td>
<td>2.68</td>
</tr>
<tr>
<td>Ni</td>
<td>0.16</td>
<td>0.14</td>
<td>0.20</td>
</tr>
<tr>
<td>Mo</td>
<td>1.80</td>
<td>5.0</td>
<td>1.20</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.11(a): Results from FEGSTEM-EDS microanalysis of 2½Cr1Mo steels (from Vorlicek and Flewitt [77])
Table 5.11(b): Results from FEGSTEM-EDS microanalysis of Magnox submerged arc weld metal (from Vorlicek and Flewitt[77]).

The weld metal was of a more complex structure than the 2⅓Cr1Mo type steels. It exhibited various grain sizes throughout its structure, and thus the results obtained from the analysis were related to the region they were taken from. The results clearly showed that phosphorus was heavily segregated to the boundaries. There did not, however, appear to be any segregation of any of the major alloying elements of the material. The results from the analysis of this material are shown in Table 5.11(b). The concentrations quoted are those obtained at the grain boundary ($C_{GB}$) and 150nm from the boundary ($C_{150}$). Note that in the larger grained material, the grain boundary enrichment of phosphorus is of the order of 10 times bulk concentration, whereas the smaller grained material only exhibited enrichments of 4 times.

The most recent observations of TNES were obtained by Cowan[78] from an Fe-P-C model alloy. A number of specimens were aged at 600°C for 20 hours to attain equilibrium phosphorus segregation. Following ageing, the samples were then cooled at different rates to room temperature. The cooling processes used were water quenching, air and furnace cooling. Following cooling, the samples were analysed using AES to determine the phosphorus and carbon concentrations on the grain boundaries. To determine the grain boundary concentrations of phosphorus and carbon during the cooling process, the samples were either air or furnace cooled to a reference temperature, and then water quenched to room temperature. The results from these analyses for both air and furnace cooling from 600°C are shown in Figures 5.13 and 5.14.
Figure 5.13: Phosphorus and carbon grain boundary segregation during air cooling (from Cowan[78])

Figure 5.14: Phosphorus and carbon grain boundary segregation during furnace cooling (from Cowan[78])

It can be seen from these results that a site competition effect occurs between phosphorus and carbon. This effect has been investigated in some detail in relation to equilibrium segregation earlier in this Chapter. However, to the authors knowledge, the work...
of Cowan is the only published data of this effect in relation to non-equilibrium conditions in RPV-type steels. For both cooling processes, it would appear that at the higher temperatures, phosphorus is predominant at the grain boundaries. As the temperature drops, the higher diffusivity of carbon causes it to segregate more and, owing to the site competition effect, remove phosphorus from the grain boundary.

5.3.2 Theoretical models for TNES

There are two schools of thought in modelling the non-equilibrium segregation of impurity atoms to grain boundaries. The first to be discussed will be an analytically based model, which extends the theory of equilibrium segregation described earlier. The alternative approach is termed the Inverse Kirkendall model, which will briefly be discussed in Section 5.3.2.5. The analytically based model will be used subsequently to obtain predictions for the thermal heat treatments that the RPV steel underwent after constructions. These predictions will be presented alongside those obtained from the thermal equilibrium segregation models, with the aim of gaining a more thorough understanding of the state of the material prior to entering service.

5.3.2.1 Thermodynamics of the analytical modelling of TNES

The theory of non-equilibrium segregation was originally developed by Aust and co-workers\(^79\) and Anthony\(^80\). The theory proposed the formation of freely migrating bound complexes between vacancies and impurity atoms during rapid cooling. These complexes were assumed to have sufficient long-range mobility to be able to migrate to grain boundaries. This migration behaviour would be governed by the variation in vacancy concentration that is created adjacent to grain boundaries when a material is rapidly cooled.

During cooling, the thermal equilibrium concentration of vacancies falls. However, this thermal equilibrium concentration of vacancies can only be maintained at vacancy sinks, for example, grains boundaries and surfaces. In the bulk of the material, far from these vacancy sinks, the concentration of vacancies remains at the super-saturation concentration that was created whilst the material was at the higher temperature. Thus, there is a gradual change in the concentration of vacancies between the bulk material and the vacancy sinks. Vacancies will diffuse along this gradient from the bulk material to the vacancy sink in order to eliminate this concentration variation. Therefore, if there is an attractive force between vacancies and impurity atoms, such as in the form of freely-migrating bound complexes, then these too will migrate along these vacancy concentration gradients.

However, the original concentration of isolated impurity atoms remains constant throughout the grain. Thus, any vacancy-impurity complexes that migrate toward the vacancy sink will cause the concentration of impurity atoms to increase at these sinks. The magnitude of this impurity atom concentration will therefore be related to the vacancy concentration gradient due to the rapid cooling process. However, this increase in the impurity
concentration relies on the assumption that the diffusion of bound vacancy-impurity atom complexes is quicker than the diffusion of the impurity atoms alone. Should this not be the case, there would be no enrichment of impurity atoms at the vacancy sinks.

Since this whole process occurs during a rapid quenching operation, any subsequent isothermal heat treatments may cause the impurity atoms to become sufficiently mobile to move away from the grain boundary region. This will therefore reduce the extent of the segregated region, and eventually the material will return to its original equilibrium condition. This latter case is termed de-segregation, and will be discussed later in relation to the kinetics of the model.

The modelling process follows a series of equations to determine both, the magnitude, and the extent of segregation. It is assumed that the material is quenched from a solution treatment temperature, $T_s$, to a temperature at which diffusion of vacancies and complexes can be assumed negligible. In the model described here, this temperature is taken to be half of the absolute melting temperature of the material, $T_{0.5T_m}$.

Firstly, it is therefore necessary to determine the equilibrium concentration of vacancies, at the solution treatment temperature, $T_s$, and the diffusion cut-off temperature, $T_{0.5T_m}$. Following the calculation of these values, it will be possible to determine the concentration of vacancy-impurity complexes at these temperatures. Finally, the ratio of the complex concentration at the two different temperatures will determine the magnitude of the segregation of the impurity atoms to the grain boundaries.

The concentration of vacancy-impurity atom bound complexes, $C_c$, at any absolute temperature, $T$, can be determined from:

$$C_c = k_c C_v C_i \exp\left(\frac{E^v}{kT}\right)$$

(5.9)

where: $k_c$ is a geometrical constant.

$C_v$ is the thermal equilibrium vacancy concentration, from $C_v = k_v \exp\left(-\frac{E^v}{kT}\right)$

$k_v$ is a geometrical constant

$E^v$ is the thermodynamic free energy of vacancy formation.

$C_i$ is the impurity element concentration.

$E^c$ is the thermodynamic free energy of vacancy-impurity complex binding.

Expansion of this equation allows it to be re-written as:

$$C_c = k_c k_v C_i \exp\left(\frac{E^v - E^c}{kT}\right)$$

(5.10)

Theoretically, it has been assumed that the cooling between the solution treatment temperature, $T_s$, and the diffusion cut-off temperature, $T_{0.5T_m}$, is instantaneous. Therefore,
the ratio of the complex concentration, $C_c$, to the impurity element concentration, $C_i$, at both temperatures determines the magnitude of segregation. This figure is the maximum level of segregation that can be reached at the grain boundary. This can be expressed as:

$$\frac{(C_i/C_c)_{T_{s\text{STM}}}}{(C_i/C_c)_{T_s}} = \exp\left[\frac{(E_{\text{b}} - E_f)}{kT_s} - \frac{(E_{\text{b}} - E_f)}{kT_{0.5T_m}}\right]$$  \hspace{1cm} (5.11)

However, this equation predicts that as the vacancy-impurity complex binding energy term increases, the magnitude of segregation will decrease. This is clearly incorrect, since any impurity species that binds more strongly to a vacancy is more likely to contribute to the overall segregation behaviour. Therefore, the inclusion of a term to correct for the absolute concentration of complexes is required. This term is taken to be the ratio of the vacancy-impurity complex binding energy to the vacancy formation energy. The modified equation can be expressed in terms of the bulk and grain boundary concentrations of the impurity atoms, thus:

$$\frac{C_b}{C_g} = \frac{(E_{\text{b}})}{(E_f)} \exp\left[\frac{(E_{\text{b}} - E_f)}{kT_s} - \frac{(E_{\text{b}} - E_f)}{kT_{0.5T_m}}\right]$$  \hspace{1cm} (5.12)

where: $C_b$ is the grain boundary impurity concentration.
$C_g$ is the concentration of impurity atoms in the bulk of the material.

In contrast to the approach just described, Song and Xu\[^{[82]}\] suggested that the temperature at which diffusion ceases is at 600°C. This is slightly different to the cut-off temperature of half of the melting temperature, assumed by the model of Faulkner. This difference corresponds to a difference of around 150°C, assuming the melting temperature of steel is taken as approximately 1500°C.

5.3.2.2 Kinetics of TNES

The magnitude of TNES, given by Equation (5.12) does not take into account any kinetic effects, and therefore assumes that the process occurs instantaneously. The kinetic modelling of TNES relies on the determination of an effective time for the cooling process, which then permits calculations for various diffusion coefficients to be performed at one, constant temperature. In the model presented here, the starting temperature of the process, $T_s$, is used as the reference temperature.

The original approach to determining the effective quench time was presented by Faulkner\[^{[83]}\]. It was assumed that diffusion of vacancy-impurity atom complexes ceased at a temperature of approximately half of the melting temperature of the material, $T_{0.5T_m}$, in a similar approach to that used to predict the maximum level of TNES. Therefore, variations in both the starting temperature of the quench, and the quench rate would affect the calculated effective time. The segregating impurity species would also influence this effective time. The equation relating the effective quench time, $t_{\text{eff}}$, to a constant quench rate, $\theta$, was:
\[ t_{\text{eff}} = \frac{RkT_s^2}{\theta E_A} \]  \hspace{1cm} (5.13)

where: \( R \) is a constant (taken to be 0.01).
\( E_A \) is the average activation energy for diffusion of complexes and impurities in the matrix.

The work of Faulkner also included an approach to determining the additional effective time caused by isothermal heat treatments, following a cooling process from a higher temperature. It was assumed that the ageing temperature, \( T_A \), and time, \( t_A \), would increase the effective time. The equation to determine this effect is:

\[ t_{\text{eff}} = t_A \exp \left( -\frac{E_A(T_s - T_A)}{kT_s T_A} \right) \]  \hspace{1cm} (5.14)

Figure 5.15: Schematic of defining a variable cooling process by a number of constant-time temperature steps

Song and Xu\textsuperscript{[82]} modified this approach to consider continuously changing cooling rates. It was proposed that a cooling curve could be modelled by considering it as a number of isothermal steps, each with a constant time interval. This situation can be seen schematically in Figure 5.15. The equation to predict the effective time was an extension of Equation (5.14), thus:

\[ t_{\text{eff}} = \sum_{i=1}^{n} t_i \exp \left( -\frac{E_A(T_s - T_i)}{kT_s T_i} \right) \]  \hspace{1cm} (5.15)

where: \( t_i \) is the isothermal holding time at the \( i^{th} \) step
\( T_i \) is the temperature at the \( i^{th} \) step
This approach to determining effective times is obviously more realistic than to simply consider that the quench rate remains constant throughout the process. However, there is little subsequent work that determines effective quench times of continuously changing cooling rates. The majority of works incorporating effective time calculations simply assume that the cooling process occurs with a constant quench rate. Likewise, the effect of multiple cooling processes has received little attention. Both of these effects have been considered in the work of Faulkner, Meade and Hales\cite{84}, presented at the Institute of Materials conference entitled "Integrity of High Temperature Welds". The theoretical appraisal of both variable cooling rates and multiple cooling processes will now be presented.

From Chapter 4, it was shown that the construction of RPV's relies on the use of multi-pass submerged arc welding techniques. It is therefore highly likely that material in the heat-affected zone of such a submerged arc weld will by repeatedly heated and cooled. This thermal cycling will therefore have a cumulative effect on the segregation behaviour of the material. Therefore, if the effective time of each successive thermal cycle is considered, it will be possible to determine an overall effective time for the whole welding process. This will allow more accurate prediction of TNES within heat affected zone material.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.16.png}
\caption{Finite difference heat transfer model output (from Faulkner and co-workers\cite{84})}
\end{figure}

It is possible to accurately determine the thermal history of heat affected zones adjacent to weld material by using finite difference heat transfer models. These complex two-dimensional models consider the region of the weld and heat affected zone as a 'mesh', an example of which is shown in Figure 5.16. At the intersection of each line of the mesh, there exists a 'node', at which a series of complex rules operate to determine its thermal
behaviour. For each node of the mesh, the thermal history due to the welding process can therefore be determined. This data can then be used to more accurately predict the effective quench time by determining the exact cooling rate as a function of cooling time.

In order to calculate the effective time for nodes selected from the mesh presented, the equation of Song and Xu was extended. Firstly, it was necessary to determine an equation to match the cooling curve predicted by the finite difference model. This cooling rate equation was expressed in terms of the initial and final temperatures of the cooling process, and by dividing the total cooling process time into a number of smaller constant time intervals. It was therefore found possible to calculate the cooling rate at the $i$th time interval from the following equation.

$$
\theta_i = \left( \frac{T_s - T_0}{\tau} \right) \exp \left( -\frac{1}{\tau} \right)
$$

(5.16)

where: $T_s$ is the starting temperature of the quench process.

$T_0$ is the final temperature of the quench process.

$\tau$ is related to the total quench time by $\tau = \frac{t^2}{10}$

$t$ is the overall cooling time.

Having predicted the cooling rate for the $i$th time interval, it is then possible to determine the temperature changes that occurs. These temperatures can then be substituted into the following equation, which is used to determine the increase in the effective quench time.

$$
\text{teff} = \text{teff}(i-1) + \sum_{i=1}^{n} \theta_i \exp \left( -\frac{E_a(T_s - T_0)}{kT_sT_i} \right)
$$

(5.17)

This equation can then be used to determine effective times of subsequent cooling processes, and the sum of the times can be used to predict the TNES due to the overall process. When considering a number of subsequent cooling processes, the calculations must be performed at the highest temperature, since this will determine the maximum level of grain boundary segregation from Equation (5.12).

**Determination of segregation profiles adjacent to grain boundary**

To determine the extent of segregation, the diffusion of the impurity atoms and vacancy-impurity atom complexes during the effective quench time must be considered. This situation has been considered theoretically by a number of workers\textsuperscript{[81,82,85]}. In the work of Faulkner\textsuperscript{[81]}, an approach was presented to determine the extent of TNES by using the solution of Fick's Second Law of diffusion for semi-infinite solids. This solution can be expressed as:
where: \( C_x \) is the impurity concentration at a distance, \( x \), from the grain boundary
\( D_{ct} \) is the diffusion coefficient of the vacancy-solute complexes at the solution treatment temperature.

The type of segregation profile obtained from this approach can be seen in Figure 5.17. With increasing effective times, the width of the segregated impurity atom layer increases, owing to increased diffusion of complexes toward the grain boundary. This method, however, does not correctly predict the actual state of affairs adjacent to grain boundaries. With increasing time, impurity atoms will become enriched adjacent to the grain boundary, as predicted by the solution to Fick's Second Law. However, outside of this segregated zone, there will be a region of impurity depletion, from which the impurity atoms will have segregated to cause the enriched layer adjacent to the boundary. The reason for the lack of a depleted region in this modelling approach is the assumption of a semi-infinite source of segregant which is able to take part in diffusion towards the grain boundary.

![Figure 5.17: TNES concentration profile from Faulkner’s model](image)

Most recently, Jiang and Faulkner\(^{[86]}\) presented a more rigorous method of determining the segregation profile adjacent to a grain boundary. This theory was originally incorporated into a model that considered the precipitation behaviour of aluminium alloys. The precipitation modelling aspect of Jiang and Faulkner's work has since been extended, and will be presented in Chapter 7. The segregation modelling aspect of their work will be presented here.

The limitation of the approach described previously was that it failed to predict the region of impurity depletion adjacent to the segregated layer. Jiang and Faulkner therefore assumed that two regions, the solute concentrated layer (SCL), and the solute depleted layer (SDL), are created near to the boundary, as shown in Figure 5.18. These originate from solute being taken into the SCL from the bulk of the material by diffusion of vacancy-impurity
atom complexes during the cooling process. With increasing time, the widths of both of these regions become larger, owing to the increased diffusion distances of the complexes.

![Diagram showing solute concentrated layer (SCL) and solute depleted layer (SDL)](image)

**Figure 5.18: Schematic of a typical TNES enrichment profile**

As with the model of Faulkner presented previously, Jiang and Faulkner assumed that diffusion of vacancy-impurity atom complexes ceased at some temperature, which was taken to be half of the melting temperature of the alloy. Thus, during quenching from solution treatment temperature, or during high temperature ageing where the ageing temperature, \( T_a \), is greater than \( T_{0.5T_m} \), Equations (5.19a)-(5.19c) govern the segregation behaviour.

\[
\begin{align*}
\text{If } x & \leq w_{\text{SCL}} & C(x, t_{\text{eff}}) &= C_b \exp(-\alpha x^2) & \text{(5.19a)} \\
\text{If } w_{\text{SCL}} < x & \leq w & C(x, t_{\text{eff}}) &= C_b \exp(-\alpha x^2) + \frac{x-w_{\text{SCL}}}{w} C_g & \text{(5.19b)} \\
\text{If } x & > w & C(x, t_{\text{eff}}) &= C_b \exp(-\alpha x^2) + C_g & \text{(5.19c)}
\end{align*}
\]

where: \( w_{\text{SCL}} \) is the width of the solute concentrated layer, from \( w_{\text{SCL}} = \frac{C_g \sqrt{2D_c t_{\text{eff}}}}{C_b} \)

\( w \) is the total width of the segregation region, from \( w = \frac{2w_{\text{SCL}}(C_b - C_g)}{C_g} \)

\( \alpha \) is a calculation constant, from \( \alpha = \frac{\pi C_b^2}{8D_c t_{\text{eff}} C_g^2} \)

**De-segregation processes**

During fast cooling, where the effective cooling time is short, the diffusion of complexes towards the grain boundary results in impurity atoms accumulating, both on the boundary, and in a region around the boundary. However, for longer effective cooling times, the diffusion of impurity atoms back into the grain, from the grain boundary region, must be considered. The critical time at which segregation ceases and desegregation takes over is...
calculated from the relative diffusion coefficients of the bound vacancy-impurity atom complexes and individual impurity atoms. It can be determined from:  

\[ t_c = \frac{\delta^2 \ln(D_{cTS}/D_t)}{4(D_{cTS} - D_t)} \]  

(5.20)

where:  
\( \delta \) is a numerical factor.  
\( d \) is the grain size of the material.  
\( D_t \) is the impurity element diffusion coefficient.

Thus, as grain size decreases, the critical time for desegregation reduces. Conversely, as grain size increases, the critical time increases, which permits more non-equilibrium segregation to occur. The desegregation behaviour of impurity atoms is described by the thin film solution to the diffusion equation, thus:

\[ \frac{C_x - C_g}{C_b - C_g} = \left( \frac{D_{cTS}t_c}{D_t t_{eff}} \right)^{1/2} \exp \left( \frac{-x^2}{4D_{cTS}t_{eff}} \right) \]  

(5.21)

In addition, the grain boundary concentration of impurity atoms will also diminish due to desegregation. This concentration, \( C_{x0} \), can be determined from:

\[ \frac{C_{x0} - C_g}{C_b - C_g} = \left( \frac{D_{cTS}t_c}{D_t t_{eff}} \right)^{1/2} \]  

(5.22)

**Segregation during subsequent ageing processes**

The effect of both segregation and desegregation during quenching and high temperature \((T_A > T_{0.5Tm})\) has been introduced thus far. The situation of post-quench isothermal heat treatments at temperatures less than \(T_{0.5Tm}\) will now be considered. It has been shown that the width of the SCL, \(w_{SCL}\), increases with time up to the critical time for segregation. For times longer than the critical time, desegregation occurs, where the solute atoms are sufficiently mobile to diffuse away from the boundary at a greater rate than the solute atoms arriving at the boundary in the form of complexes. The magnitude of segregation at the boundary therefore decreases.

However, the situation where a post-quench heat treatment occurs at a temperature below \(T_{0.5Tm}\) needs to be considered. Since the temperature is lower than that assumed for complex migration towards the grain boundary, TNES cannot occur. It is therefore assumed that the SDL is gradually filled up by solute diffusion down the concentration gradient, formed by the cooling-induced non-equilibrium segregation process. This scenario can be shown in [Figure 5.19](#).
The equations to describe this process were presented by Jiang\cite{87}. Thus, for post-quench isothermal ageing, where the ageing temperature is less than $T_{O.S}:$

\[ C(x,t) = C_b \exp(-\alpha' x^2) \quad (5.23a) \]

\[ C(x,t) = C_b \exp(-\alpha' x^2) + c_1(x,t) + c_{II}(x,t) + c_{III}(x,t) + c_{IV}(x,t) \quad (5.23b) \]

where:

\[ c_1(x,t) = C_g \frac{(x-w_{SCL})C_g}{w} \text{erf} \frac{x-w_{SCL}}{2\sqrt{D_{CTa}t}} + \frac{2\sqrt{D_{CTa}t}C_g}{\sqrt{\pi w}} \exp \frac{(x-w_{SCL})^2}{4D_{CTa}t} \]

\[ c_{II}(x,t) = \frac{C_g}{2} \left( \text{erf} \frac{w+x-w_{SCL}}{2\sqrt{D_{CTa}t}} + \text{erf} \frac{w-x+w_{SCL}}{2\sqrt{D_{CTa}t}} \right) \]

\[ c_{III}(x,t) = \frac{D_{CTa}tC_g}{\sqrt{\pi w}} \left[ \exp \frac{(w+x-w_{SCL})^2}{4D_{CTa}t} + \exp \frac{(w-x+w_{SCL})^2}{4D_{CTa}t} \right] \]

\[ c_{IV}(x,t) = \frac{x C_g}{2w} \left( \text{erf} \frac{w+x-w_{SCL}}{2\sqrt{D_{CTa}t}} - \text{erf} \frac{w-x+w_{SCL}}{2\sqrt{D_{CTa}t}} \right) \]

$\alpha'$ can be determined from $\alpha' = \frac{\pi C_b^2}{8D_{CTa}t eff C_g^2}$

$w_{SCL}$ is the width of the solute concentrated layer, from $w_{SCL} = \frac{C_g \sqrt{2D_{CTa}t eff}}{C_b}$

$D_{CTa}$ is the diffusion coefficient of the vacancy-solute complexes at the ageing temperature.

### 5.3.2.3 Determination of vacancy-impurity complex binding energies

The TNES model described thus far has assumed the formation, and subsequent migration, of bound complexes of vacancies and impurity atoms. In order to make accurate predictions with the model, a method of determining the binding energies of these vacancy-
impurity atom complexes is required. The calculation of these binding energies takes the
derivation of Chapman and Faulkner\(^\text{[86]}\), which was extended subsequently by Faulkner and
coworkers\(^\text{[89]}\). Their approach assumes a size misfit relationship. This size misfit induces a
strain field within the matrix of the material, which in turn makes the formation of a complex energetically more attractive.

The first stage in determining the vacancy-impurity complex binding energy is to
calculate the formation energies of vacancies, di-vacancies, impurities and di-impurities. The
formation of a vacancy within a regular lattice is shown schematically in Figure 5.20, with
the nomenclature in line with that used in the following equations. Therefore, the vacancy formation energy, \(E_N\), can be determined from:

\[
E_N = E_{sv} + \frac{8\pi}{3}Gr_0(r_v - r_0)^2
\]  

(5.24)

where: \(E_{sv}\) is the internal surface energy of the vacancy, from \(E_{sv} = 4\pi r_0^2S\)

\(r_v\) is the final radius of vacancy after lattice distortion, from \(r_v = \frac{r_0}{\left(\frac{3S}{2Gr_0} + 1\right)}\)

\(S\) is the surface energy per unit area of the vacancy.
\(G\) is the shear modulus of the matrix.
\(r_0\) is the matrix atom radius.

![Lattice distortion around a single vacancy](image)

Figure 5.20: Lattice distortion around a single vacancy

The undersized impurity atom formation energy, \(E_{fu}\), is assumed to take the same
form of the equation used to predict the vacancy formation energy. This is because the
impurity atoms in the matrix are assumed substitutional impurities. Thus, instead of the
lattice deforming around the vacancy, the undersized impurity atom causes the deformation.
The di-impurity complex formation energy, $E_{fi}$, is determined from:

$$E_{fi} = 2E_{si} + \frac{14\pi}{3}Gr_0(r_i - r_0)^2 \tag{5.26}$$

Figure 5.21: Lattice distortion around vacancy-impurity complex

The work of Chapman assumed that the formation energy of a vacancy-impurity atom complex could be modelled by removing an impurity atom from a di-impurity atom complex, and letting the vacancy equilibrate, shown in Figure 5.21. Thus, the formation energy of a vacancy-impurity atom complex can be expressed as:

$$E_{vi} = E_{fi} - E_{si} + 4\pi r_v^2S + \frac{8\pi}{3}Gr_0(r_v - r_0)^2 \tag{5.27}$$

where: $E_{si}$ is the interfacial energy of the removed impurity atom.

The binding energy of these vacancy-impurity atom complexes, $E_{vi}$, is equal to the difference between the formation energies of the vacancy, impurity and vacancy-impurity complex, thus:

$$E_{vi} = E_{fi} + E_{vi} - E_{vi} \tag{5.28}$$

The graph shown in Figure 5.22 plots the vacancy-undersized impurity atom binding energy as a function of the impurity atom radius for a ferritic steel matrix. The calculations to determine the complex binding energy for oversized impurity atoms requires the use of modified equations to those presented here. The determination of these equations can be found in the work of Faulkner and co-workers\(^{[49]}\).
Figure 5.22: Binding energies of vacancy-solute complexes in a ferritic steel matrix (from Faulkner and co-workers[89])

5.3.2.4 Migration of vacancy-solute bound complexes

The theoretical models for both TNES, presented in this Chapter, and RIS, discussed in Chapter 6, assume that the segregation mechanism is the diffusion of bound complexes of solute atoms and lattice point defects towards grain boundaries. In the case of TNES, the freely migrating bound complex is assumed to comprise a substitutional solute atom and a vacancy. The RIS mechanism of segregation assumes the bound complex exists between a solute element and an interstitial atom. This section will concentrate of the vacancy-solute complex.

Vacancy-solute complexes are formed when an isolated vacancy and a solute atom occupy nearest neighbour sites in the matrix. The binding energy for this complex geometry is therefore the sum of the free energy difference of the lattice between the vacancy- and solute- occupied sites. Theoretical calculations to obtain these values are presented in the following section.

The process of migration of these complexes is still a matter of discussion in the literature, although there is some agreement between the various workers. The actual migration mechanism of the vacancy-solute bound complex species will affect the energy of migration. One possible mechanism for migration of these complexes is shown in Figure 5.23 for complex migration through a bcc matrix, where the solute atom is represented by the black circle, and the vacancy by the open square. The complex starts at the position shown in 5.23(a), with the solute atom and vacancy occupying nearest neighbour sites. The
vacancy then jumps position, and the complex therefore assumes the position shown in 5.23(b). The solute and vacancy then swap positions, shown in 5.23(c), and the process can then start again. In this example, the complex does not dissociate, since at all stages, the vacancy and solute atom remain at nearest neighbour locations.

However, this mechanism is energetically quite difficult. The vacancy jump shown between 5.23(a) and 5.23(b) is between lattice sites that are only secondary neighbours. Therefore, the vacancy jump energy that is required in overcoming the barrier is high.

![Figure 5.23: Migration of vacancy-solute complexes assuming complex cannot dissociate (from Song[90])](a)(b)(c)

A second mechanism for migration can therefore be considered, in which the solute and vacancy jumps are restricted to nearest neighbour locations. However, in this case, the complex must partially dissociate. The starting positions of the vacancy and solute atom are shown in Figure 5.24(a). Again, the solute atom is represented by the solid circle and the vacancy by the open square. The movement of the vacancy to the position shown in 5.24(b) causes the complex to dissociate, since the positions occupied by the solute atom and vacancy are no longer nearest neighbour. The vacancy then jumps to the position shown in 5.24(c), which now recombines the complex again by returning it to nearest neighbour sites. The final step is the swapping of position of the solute and vacancy, shown in 5.24(d).

The exact mechanism by which the vacancy-solute bound complex migrates is dependent upon the binding energy of the complex, together with the vacancy migration energy. In the first example, the overall energy required by the process is the sum of the vacancy migration energy between secondary nearest neighbour locations and the vacancy-solute atom exchange energy. The migration energy of the second mechanism is equal to that of twice the vacancy migration energy, plus the vacancy-solute complex binding energy and the vacancy-solute atom exchange energies.
5.3.2.5 Inverse Kirkendall model of non-equilibrium segregation

An alternative approach to modelling the process of TNES is the Inverse Kirkendall model. This model has been well documented with regard the phenomenon of radiation-induced segregation, and a more comprehensive discussion will be given in Chapter 6. However, it is worth mentioning here the limited theoretical work that has been developed in this particular area.

The particular paper that will be discussed in this section was written by Karlsson[73]. This paper was one of a series of papers published discussing the non-equilibrium segregation of boron in austenitic stainless steel[71,72,74]. Some of the experimental results that were presented in this work have already been discussed in the earlier section of this Chapter.

Mathematically, the model can be described by the coupled diffusion equations of Fick’s second law for vacancies, boron atoms and vacancy-boron complexes, as shown in Equations 5.29(a) to (c).

\[
\frac{\partial C_v}{\partial t} = D_v \frac{\partial^2 C_v}{\partial x^2} \quad (5.29a)
\]

\[
\frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial x^2} \quad (5.29b)
\]

\[
\frac{\partial C_{vb}}{\partial t} = D_{vb} \frac{\partial^2 C_{vb}}{\partial x^2} \quad (5.29c)
\]

where:
- \( C_v \) is the thermal equilibrium concentration of vacancies.
- \( C_b \) is the thermal equilibrium concentration of boron atoms.
- \( C_{vb} \) is the thermal equilibrium concentration of vacancy-boron complexes.
- \( D_v \) is the vacancy diffusion coefficient.
- \( D_b \) is the boron (impurity element) diffusion coefficient.
- \( D_{vb} \) is the vacancy-boron complex diffusion coefficient.
- \( x \) is the distance from the vacancy sink.
The boundary conditions that were applied to the model were dependent upon the species being considered. For vacancies, the grain boundaries were assumed to be perfect sinks, i.e. the grain boundary concentration of vacancies always remained at the thermal equilibrium concentration. For boron, two boundary conditions were considered. In the first case, it was assumed that the grain boundaries could not bind the boron atoms, so that it was possible for the boron to migrate away. The alternative boundary condition was that the boron atoms at the boundary were bound, i.e. the boundary was a perfect boron atom sink as well as being a perfect vacancy sink. In the model, diffusion parameters were assumed to be concentration and temperature independent, and precipitation effects were neglected. Additionally, cooling rates were assumed constant, and the composition at the grain centres was assumed constant, i.e. $\delta C/\delta x=0$.

However, although the equations themselves appear to be fairly straightforward, there are no exact solutions to them, since the diffusion coefficients and boundary conditions vary with time. In order to calculate the segregation profiles, an iterative method called the finite difference method is used. In this method, the derivatives above are expressed as finite differences by using Taylor series in time and distance, thus:

$$C(x, t + \Delta t) = C(x, t) + r[C(x + \Delta x, t) - 2C(x, t) + C(x - \Delta x, t)]$$ (5.30)

where: $r$ is a constant, related to the required accuracy of the results and the available computing power, and is equal to $r = D_0 \left( \frac{\Delta t}{\Delta x^2} \right)$

Some of the results presented by Karlsson are shown in Figures 5.25 and 5.26. Figure 5.25 relates the concentration profiles of the three segregating species. It can be seen that the vacancy and vacancy-boron complex profiles both follow the same trend. Figure 5.26 illustrates the effect of the cooling rate on the predicted segregation profile for boron. At low rates, the profile simply shows enrichment at the boundary. However, as the cooling rate increases, the width of this enriched region becomes narrowed, and at a rate of 100°C/s, this enriched region is bounded by a depleted region. In addition, as the cooling rate increases, the width of both the enriched and depleted regions decrease.

The application of rate theory Inverse Kirkendall modelling to prediction of TNES has also been discussed by Simonen and Bruemmer[91]. The discussion highlighted the sensitivity of the modelling approach to changes in the values of the input parameters, as well as discussing the predictions in relation to a range of quench rates. Owing to time constraints, however, further appraisal of the modelling technique was not feasible, and therefore this brief discussion is presented purely as an introduction to the theoretical model and its predictions.
Figure 5.25: Predictions for TNES of boron in austenitic steel using Rate Theory model of Inverse Kirkendall type segregation (from Karlsson\textsuperscript{[73]})

Figure 5.26: Simulated segregation profiles for different cooling rates (from Karlsson\textsuperscript{[73]})
5.4 Theoretical predictions for post-weld heat treatment

Thus far in the Chapter, experimental observations of both TES and TNES have been discussed, and the modelling approaches have been presented. Owing to the complex nature of the post-weld heat treatments that the RPV shell material has been subjected to, it is best that the predictions for both TES and TNES are discussed together. Recalling the heat treatment data given in Chapter 4, it is apparent that during the heat treatment process, both equilibrium and non-equilibrium processes can occur. The basic heat treatment of the materials consists three distinct phases. The first phase consists of heating the material to 920°C, where it is held for 6 hours, and then rapidly quenched. Owing to the high temperature at which the material is held, little equilibrium segregation could occur. However, the rapid cooling of the material from this high temperature will introduce a significant level of non-equilibrium segregation into the material.

The second phase of the basic heat treatment process consists of heating the material to 600°C, where it is held for 41.5 hours, followed by a slow cool to room temperature. The duration and temperature of this tempering process would be expected to induce a significant amount of equilibrium segregation into the system. This effect will therefore be modelled. The third phase of the heat treatment is a shorter period temper, although at a higher temperature. In the case of the basic heat treatment process, this third phase is a 6-hour temper at 650°C. Again, this temper could be expected to induce equilibrium segregation into the material.

5.4.1 Theoretical predictions of TES

Within the context of this project, work has been carried out to examine both theoretically and experimentally the equilibrium segregation behaviour of the impurity elements found in the pressure vessel steels under consideration.

5.4.1.1 Modelling parameters

The parameters required for modelling the effect of TES in ferritic steel alloys are shown in Table 5.12. The parameters required relate to the diffusion of the solute atoms within the matrix, together with the solute-boundary binding energies. The concentrations of the elements are quoted in Table 4.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>P</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy for solute diffusion in ferrite, $E_S$ (eV)</td>
<td>2.68 $^{[92]}$</td>
<td>0.83 $^{[93]}$</td>
</tr>
<tr>
<td>Pre-exponential for solute diffusion in ferrite, $D_{cs}$ (m$^2$·s$^{-1}$)</td>
<td>7.12x10$^{-3}$ $^{[92]}$</td>
<td>3.94x10$^{-7}$ $^{[93]}$</td>
</tr>
<tr>
<td>Solute-boundary binding energy, $Q$ (eV)</td>
<td>0.459 $^{[98]}$</td>
<td>0.829 $^{[44]}$</td>
</tr>
<tr>
<td>Chemical phosphorus interaction coefficient (eV)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 5.12: Data for phosphorus and carbon in ferritic low-alloy steel
Parameter | Mo | Mn
--- | --- | ---
Activation energy for solute diffusion in ferrite, $E_s$ (eV) | 2.51 \cite{93} | 2.60 \cite{93}
Pre-exponential for solute diffusion in ferrite, $D_{os}$ (m² s⁻¹) | 3.467 x 10⁻⁴ \cite{93} | 7.2 x 10⁸ \cite{93}
Solute-boundary binding energy, $Q$ (eV) | 0.00104 \cite{66} | 0.083 \cite{66}
Chemical phosphorus interaction coefficient (eV) | 1.835 \cite{66} | 0.4375 \cite{66}

Table 5.12: Data for molybdenum and manganese in ferritic low-alloy steel

5.4.1.2 Binary TES model

The binary model that has been used to model equilibrium segregation follows from the work of McLean and Guttmann, described in detail in an earlier section. Equilibrium segregation will be anticipated to occur, since the materials used in the construction of the reactor pressure vessel will be experiencing temperatures of between 250 and 315°C for a period of many years. However, this temperature is low for any significant segregation to occur. As mentioned earlier, equilibrium segregation of phosphorus has been known for many years as 500°C embrittlement. Thus, at the lower temperatures of the reactor operating temperatures, we should expect only slight segregation. The predictions obtained from the model are shown in Figure 5.27.

![Figure 5.27: Predictions for TES as a function of temperature for phosphorus after 6 hours and 41.5 hours](image-url)
5.4.1.3 Ternary TES model

As with the work of Guttmann, ternary equilibrium segregation needs to be accounted for, since there are many alloying elements present that could co-segregate and cause different predictions than the simplified binary model would give. From the literature, it has been shown that molybdenum, manganese and chromium all interact with phosphorus, causing enhancement of the grain boundary segregation. Predictions are presented here highlighting the influence of both molybdenum and manganese. Figure 5.28 shows the predictions for phosphorus and molybdenum segregation in isolation after 42 hours. It can be seen that the molybdenum has a very low affinity to segregate to the grain boundary. However, if the interaction coefficient is incorporated into the model, the segregation of molybdenum is enhanced greatly. This effect can be seen in Figure 5.29. Additionally, the phosphorus appears to segregate more at higher temperatures owing to this interaction.

The interaction between manganese and phosphorus is less dramatic, however. Again, the predictions for both elements segregating in isolation are shown (Figure 5.30), and the segregation behaviour of manganese can be seen to be quite low, although higher than the molybdenum. However, the predictions incorporating the interaction coefficient between phosphorus and manganese show little change to the behaviours, shown in Figure 5.31. Again, the phosphorus appears to segregate more at higher temperatures owing to this interaction.

The site competition effect that occurs between phosphorus and carbon has been modelled, and predictions for an ageing time of 42 hours are presented in Figures 5.32 and 5.33. The carbon concentrations vary between the two predictions, whereas the phosphorus concentration remains constant. In Figure 5.32, the carbon concentration is that of the bulk content, which is approximately 0.2at.%. It can, however, be expected that a significant proportion of this carbon will be tied up in precipitates, and will therefore be taken out of solution. Therefore, predictions are presented for a reduced carbon content of 0.02at.%, shown in Figure 5.33.
Figure 5.28: Predictions for molybdenum and phosphorus segregation after 42 hours assuming no interaction

Figure 5.29: Predictions for molybdenum and phosphorus segregation after 42 hours with interaction
Figure 5.30: Predictions for manganese and phosphorus segregation after 42 hours assuming no interaction

Figure 5.31: Predictions for manganese and phosphorus segregation after 42 hours with interaction
Figure 5.32: Grain boundary concentration of Phosphorus and Carbon after 42 hours allowing for site competition (0.041 at% P, 0.2 at% C)

Figure 5.33: Grain boundary concentration of Phosphorus and Carbon after 42 hours allowing for site competition (0.04 at% P, 0.02 at% C)
5.4.2 Theoretical predictions of TNES

Modelling the effect of TNES has been shown to be critical on the determination of the effective quench time, \( t_{eff} \). In the model, a new approach has been developed to predict these effective times for processes where the cooling rates are exponential. The predictions made here for the TNES in the material will be based on this new approach, and comparisons with the assumption of linear quench rates will be drawn.

5.4.2.1 Model parameters

The parameters used in the TNES model are shown in Table 5.13. The parameters for phosphorus segregation in a ferritic matrix are quoted. The appropriate references for the parameters are also quoted in the Table. An additional parameter is the self-diffusion in \( \alpha \)-Fe, which is equal to 2.91eV [93].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( P ) in ferrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-exponential constant for vacancy-phosphorus complex diffusion (m(^2) s(^{-1}))</td>
<td>1.7x10(^{-5}) [92]</td>
</tr>
<tr>
<td>Vacancy-phosphorus complex migration energy (eV)</td>
<td>1.60 [92]</td>
</tr>
<tr>
<td>Vacancy formation energy (eV)</td>
<td>1.4 [94]</td>
</tr>
<tr>
<td>Vacancy migration energy (eV)</td>
<td>1.24 [92]</td>
</tr>
<tr>
<td>Phosphorus-vacancy complex binding energy (eV)</td>
<td>0.36 [89]</td>
</tr>
</tbody>
</table>

Table 5.13: Parameters used in theoretical model

5.4.2.2 Model predictions

The first phase of the post-weld heat treatment is a water-spray quench of the RPV cylinder shell from 920°C to 300°C, at an overall rate of 136°C per hour. This gives an approximate quench time of 4 hours 15 minutes. Using the exponential quench rate model, this cooling process can be shown by Figure 5.34. The cooling curves for the final two phases of the heat treatment process are not shown, however. Recalling the theoretical appraisal of TNES, it was assumed that TNES occurred during rapid cooling from a high temperature to a temperature at which segregation kinetics were assumed to cease. This temperature was taken as half of the melting temperature of the material. The final phases of the heat treatment of the material occur at 600 and 650°C. Thus, any segregation due to TNES during cooling from these temperatures is highly unlikely.

The effective time of this quench from 920°C to 300°C has been calculated to be 206 seconds at 920°C. Using the critical time equation for desegregation shows that at 920°C, desegregation would occur after 47 seconds. The segregation profile adjacent to the grain boundary at this critical time can be seen in Figure 5.35. It can be seen that the width of the solute concentrated layer adjacent to the grain boundary is of the order of 3000nm wide, and that the solute depleted layer extends to a distance of 30000nm from the grain boundary. However, since the calculated effective time of the cooling process is over 6 times
longer than the critical time, the effects of desegregation of solute away from the grain boundary are dominant. Therefore, any segregation due to TNES can be assumed negligible.

Figure 5.34: Predicted temperature/time plot for spray water quench from 920 to 300°C

Figure 5.35: Predicted segregation profile due to TNES at critical desegregation time at 920°C
5.5 Chapter summary

This Chapter has introduced the various theoretical models that have been employed in order to predict the behaviour of phosphorus during both post weld heat treatments and isothermal ageing processes. The segregation predictions presented are for phosphorus in A533B type ferritic steel. It has been shown that considerable phosphorus segregation can be expected due to the isothermal tempering processes. It has also been shown that the predicted molybdenum grain boundary segregation is enhanced in the presence of phosphorus, whereas there is only a negligible effect on the predicted segregation of manganese.

Predictions for the thermal non-equilibrium segregation are also presented, using a newly extended approach to determining cooling processes and effective quench times. Predictions indicate that little phosphorus segregation during quenching occurs, owing to the effects of segregation and subsequent desegregation.

The determination of the vacancy-solute complex binding energies is presented. In the following Chapter, discussing the segregation of impurity elements due to irradiation, these parameters will be extended to consider the solute-interstitial complexes that control this segregation process.
Chapter 6: Radiation Induced Segregation

6.1 Introduction

In Chapter 5, the phenomenon of thermally induced non-equilibrium segregation was discussed, both experimentally and theoretically. The phenomenon occurs when a material is experiencing conditions that are causing it to be under a continual state of microstructural change. It was shown that by quenching a material, a super-saturation of vacancies would be created within the matrix of the material. The vacancy concentration at the grain boundary, however, would remain at the thermal equilibrium concentration. A concentration gradient would therefore exist between the grain interior and the grain boundary. This gradient would act as a driving force for the migration of bound vacancy-impurity complexes, causing the enrichment of the impurity element at the grain boundary.

In this Chapter, the segregation of elements due to irradiation conditions, more commonly referred to as Radiation Induced Segregation (RIS), will be presented. Although these conditions are essentially non-equilibrium (radiation induced segregation can be assumed to be a class of non-equilibrium segregation), the phenomenon is such that it deserves to be discussed separately from thermal non-equilibrium segregation.

In ferritic steels, phosphorus and carbon will segregate to grain boundaries. Phosphorus has been the subject of many studies investigating embrittlement and equilibrium segregation, discussed previously in Chapter 5. Likewise, carbon is an active segregant in many alloy systems, as shown by its propensity to form carbides, both inter- and intra-granularly. Carbon will also act to improve the cohesive bonding of the grain boundary region, and counteract to some extent the embrittling effect of phosphorus. When considering alloys used in the construction of reactor components, in particular the reactor pressure vessel, the segregation effects of both phosphorus and carbon, as well as other alloying element interactions, must be therefore be considered. Since the reactor will be operating for a number of years, it is to be expected that equilibrium segregation will occur within the materials. However, radiation induced segregation will also occur, and the effect will be additive to any equilibrium segregation that is occurring.

In austenitic stainless steels experiencing continual irradiation, chromium has been shown to desegregate from the grain boundary, even when the boundary region has become enriched with chromium following quenching, and the accompanied process of TNES. The depletion of chromium causes the grain boundaries to become more susceptible to intergranular corrosion, more commonly referred to as Irradiation Assisted Stress Corrosion Cracking (IASCC). Although austenitic alloys are of limited relevance to this thesis, the phenomenon of IASCC is worth discussing in some detail, since it is an effect directly attributed to radiation induced segregation.
This Chapter will introduce the concept of radiation induced segregation. Firstly, a review of the current literature will be presented and discussed. This discussion will highlight the experimental observations of RIS in a range of alloy systems, illustrating the techniques that have been employed to obtain reliable data. Many of these techniques have been discussed in detail in Chapter 3, and their advantages and limitations should now be apparent. Following the review section, the various radiation induced segregation theories will be introduced. Although markedly similar to the theories used to predict thermally induced non-equilibrium segregation, the theories are fundamentally different, in both their assumptions and their predictions. Both analytically based and Inverse Kirkendall-type models will be presented. The analytical model will be described in considerable detail, since the model has been extended considerably. Results from this extended model will finally be presented, and comparison with the experimentally observed segregation data will be made.

6.2 Review of the literature

Experimentally, there has been a considerable amount of work published investigating the radiation induced segregation phenomenon, in both ferritic RPV steels, and austenitic stainless steels used for many in-core reactor components. This review will introduce a few key articles, starting with early observations of RIS, and then moving on to a discussion of observations within a range of alloy systems.

One of the earliest pieces of work investigating the segregation of elements in irradiated materials was performed by Okamoto and Wiedersich in 1974. It was realised that under irradiation, materials were subjected to a process that produced point defects. These point defects would, in turn, diffuse to both internal and external surfaces, causing a kinetic, non-equilibrium segregation of alloying elements. The amount of segregation far exceeded that predicted by the process of thermal equilibrium segregation and the theory determined by McLean.

This particular work examined the behaviour of 18Cr-8Ni-1Si austenitic stainless steel. The samples were irradiated with 3.25MeV Ni+ ions to a dose of 60dpa at a depth of 6000 angstroms from the sample surface. These irradiation conditions correspond to a surface dose of 15dpa and a dose rate of 10^-3 dpa/s. The irradiation temperature was 600°C.

The technique of Auger Electron Spectroscopy was used to examine the surface of the samples. The spectra obtained from both the irradiated and un-irradiated samples showed a number of trends. Firstly, it appeared that in the spectra obtained from the un-irradiated sample, there were no silicon peaks, and that the nickel peaks are quite low. The un-irradiated sample also showed a large concentration of chromium at the surface.

After irradiation, the chromium peak appeared to have virtually disappeared, indicating that there had been some desegregation of this element. The more pronounced nickel peak indicated that there had been some segregation to the surface of this element.
Likewise, the appearance of silicon peaks suggested that some segregation of this element occurred during irradiation as well. Of these elements, chromium can be considered an oversize solute atom relative to the matrix material, whereas both silicon and nickel, which were seen to segregate to the surface, are both undersize solute atoms compared to the matrix material. Similar observations of segregation were also reported in electron-irradiated austenitic stainless steel at void surfaces.

Following the work of Okamoto and Wiedersich, there has been a wide range of work published, investigating RIS in many different alloys, as well as examining how different irradiation conditions influence the mechanism. There have also been considerable advances in the techniques that have been employed to examine segregation within materials. Recalling the discussion of experimental observations of thermally induced segregation, the majority of the analyses were performed using AES. This technique, when combined with material removal by sputtering, can indicate the extent of segregation at grain boundaries, as well as the thickness of the segregated layer. Likewise, the technique can be used to analyse surfaces and their composition, as illustrated by the work of Okamoto and Wiedersich just discussed.

However, in order to examine the grain boundary plane, the technique relies upon the intergranular fracture of samples. Therefore, samples that fail intra-granularly cannot be analysed for grain boundary segregation, since the fracture surface will not contain exposed grain boundaries. In addition, in samples in which grain boundaries are exposed, they may not necessarily be typical of all of the grain boundaries within the bulk material.

Additionally, the size of the samples needs to be considered. When dealing with irradiated materials, it is necessary to keep the volume of material to a minimum in order to prevent any harmful effects due to residual activity. Therefore, techniques that can analyse small volumes of material will be preferential over the more traditional technique of AES. Handling of smaller samples is also therefore easier, again, due to the residual activity of the samples. A number of papers have been written on the subject of the use of high-resolution electron microscopy in radiation damage studies\[97,101-103]\. These discuss the relative merits of a range of techniques that are employed in irradiation studies, and should therefore be referred to for a more detailed explanation of the various techniques.

6.2.1 Observations of RIS in ferritic RPV steels

There has been considerable work published examining the performance and behaviour of Russian RPV steels\[36,104-111]\. In comparison, the available literature regarding irradiation-induced segregation within ASME A533B RPV steels is relatively scarce. However, there are some useful comparisons to be drawn from examination of both types of material. The literature discussing the Russian grade material will be discussed first, following which comparison with the Western materials will be made.
Miller and co-workers\textsuperscript{[36,107]} examined samples of irradiated Russian pressure vessel steel weld using atom probe field ion microscopy. Recalling the discussion in Chapter 3, this technique offers excellent resolution and the ability to examine fine scale structure. The materials examined were 15Kh2MFA Cr-Mo-V and 15Kh2NMFA Ni-Cr-Mo-V steels taken from Russian VVER 440 and VVER 1000 type nuclear reactors. The elemental compositions of the steels are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>VVER440</th>
<th>VVER1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>2.77</td>
<td>2.48</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.39</td>
<td>0.34</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.33</td>
<td>0.11</td>
</tr>
<tr>
<td>Copper</td>
<td>0.30</td>
<td>0.05</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.07</td>
<td>1.15</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.36</td>
<td>0.41</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.36</td>
<td>0.49</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.67</td>
<td>0.79</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.032</td>
<td>0.016</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.052</td>
<td>0.009</td>
</tr>
</tbody>
</table>

**Table 6.1: Composition (at.\%) of the VVER pressure vessel steels analysed by Miller and co-workers\textsuperscript{[107]}**

Although these Russian pressure vessel steels have different compositions to the materials used in Western nuclear pressure vessel reactors, they have been shown to suffer from temper embrittlement following irradiation. This observation has been assumed to be due to grain boundary segregation of phosphorus, although the phosphorus contents are lower than those quoted for ASME A533B steel.

The results from the atom probe analyses showed that prior to irradiation, the phosphorus coverage at the grain boundaries was typical of equilibrium type segregation. The phosphorus was confined to an extremely narrow region either side of the boundary indicative of monolayer coverage. However, after irradiation, the phosphorus coverage was dramatically higher. In the weld material examined, the phosphorus monolayer coverage at the grain boundary had an average of 11% prior to irradiation, and this figure went up to 24% monolayer coverage after irradiation.

More recently, Nikolaeva and co-workers\textsuperscript{[111]} have performed analyses on VVER-type RPV steels that were irradiated to a range of neutron fluences. The fluence range was between 14 and 65x10\textsuperscript{22}n/m\textsuperscript{2} (E>0.5MeV), at a temperature of 275\textdegreeC, for a period of 60000 hours. The work examined the fracture behaviour of the material and its change due to irradiation. It was found that at the low fluence irradiation, the 47J temperature shift was 165\textdegreeC. However, the high fluence irradiation induced a temperature shift of 310\textdegreeC.

Examination of the fracture surfaces illustrated the pronounced fracture change. The high fluence irradiation caused the samples to fracture, whereby 80 percent of the visible
fracture surface exhibited intergranular facets. However, at the lower fluence, the fraction of intergranular fracture was two times less. In comparison, the un-irradiated material only exhibited small areas of intergranular fracture.

Auger analysis of the exposed fracture surfaces showed that the higher fluence irradiation induced a higher degree of phosphorus segregation to the grain boundaries. The results obtained from the analysis of the complete range of irradiated samples are shown in Figure 6.1. The results are expressed in terms of a change in the phosphorus peak height ratio (PHR). This peak height ratio is determined by analysis of the Auger spectra, and is equal to the height of the phosphorus peak divided by the iron peak. It can be seen that there is an approximately linear relationship between the irradiation fluence and the change in the phosphorus peak height ratio.

![Figure 6.1: AES data for phosphorus grain boundary segregation (from Nikolaeva and co-workers)](image)

Moving away from the Russian RPV steel, Miller and Burke\textsuperscript{[38]} have examined both un-irradiated and irradiated ASME A533B steel, together with steel taken from the Gundremmingen KRB-A reactor. The irradiation conditions were a neutron fluence of between $2 \times 10^{21}$ and $1 \times 10^{23}$ m$^{-2}$ (E$>1$MeV), at temperature of 288°C. Compositions of the various alloys are shown in Table 6.2. Comparison with the Russian material discussed previously, whose compositions are shown in Table 6.X, a number of differences can be seen. Most significantly is the difference in chromium concentrations. The Russian material contains approximately 2.5% chromium, whereas the figures quoted below indicate contents far lower. The copper concentration of the VVER1000 material is also higher than the A533B steels quoted here.
The results indicated that in both irradiated and un-irradiated conditions, there were significant enrichments of the elements phosphorus, nickel and manganese. Within the un-irradiated material thermally aged at 288°C for 566 hours, the enrichments were phosphorus 3.6x, nickel 1.6x, and manganese 2.1x. In the irradiated material, the enrichments were phosphorus 12.5x, nickel 2.2x, and manganese 1.6x.

However, although this result does indicate that irradiation enhances the enrichment of phosphorus at grain boundaries, it must be noted that the exposure time of the irradiated material was approximately 8750 hours. This is significantly longer than the thermally aged material. This longer time could induce more equilibrium segregation, which could account for the increased grain boundary concentration of phosphorus.

### 6.2.2 Observations of RIS in martensitic materials

Both martensitic and ferritic/martensitic have been the subject of a range of investigations into elemental segregation during irradiation. The following discussion will highlight a range of papers that have investigated this behaviour. This category of material is finding many applications within reactors in place of austenitic stainless steels. Ferritic/martensitic alloys offer superior swelling and thermal stress resistance, together with compatibility with liquid metals, an essential requirement for materials in breeder reactors.

Clausing and co-workers investigated segregation effects within HT-9 martensitic steel. The composition of the material is shown in Table 6.3. Small notched-bar specimens, 10mm long by 1mm square, were prepared from the alloy. The samples were then annealed, quenched and tempered prior to being irradiated. The irradiation conditions within the EBR-II reactor were 410, 520 and 565°C (±20°C) at a neutron fluence of 2.8x10^{26} n/m² for a period of 15000 hours. This fluence corresponds to an irradiation damage level of 13dpa. Thermally aged samples were also prepared for an equivalent length of time.

### Table 6.2: Compositions of ASME A533B RPV steel and steel from KRB-A reactor
(from Miller and Burke)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Type</th>
<th>Cu</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Cr</th>
<th>Si</th>
<th>P</th>
<th>C</th>
<th>V</th>
<th>Fe</th>
<th>Fluence</th>
</tr>
</thead>
<tbody>
<tr>
<td>A533B</td>
<td>Plate</td>
<td>0.10</td>
<td>0.62</td>
<td>0.86</td>
<td>0.21</td>
<td>0.07</td>
<td>0.69</td>
<td>0.034</td>
<td>0.04</td>
<td>-</td>
<td>Bal.</td>
<td>2x10^21</td>
</tr>
<tr>
<td></td>
<td>Error</td>
<td>0.03</td>
<td>0.06</td>
<td>0.08</td>
<td>0.04</td>
<td>0.07</td>
<td>0.07</td>
<td>0.015</td>
<td>0.02</td>
<td>-</td>
<td>Bal.</td>
<td>2x10^21</td>
</tr>
<tr>
<td>A533B</td>
<td>Weld</td>
<td>0.12</td>
<td>0.96</td>
<td>1.41</td>
<td>0.35</td>
<td>0.03</td>
<td>0.26</td>
<td>0.029</td>
<td>0.06</td>
<td>-</td>
<td>Bal.</td>
<td>1x10^23</td>
</tr>
<tr>
<td></td>
<td>error</td>
<td>0.02</td>
<td>0.06</td>
<td>0.07</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
<td>0.010</td>
<td>0.02</td>
<td>-</td>
<td>Bal.</td>
<td>1x10^23</td>
</tr>
</tbody>
</table>
| A533B  | Weld   | 0.06 | 0.75 | 1.23 | 0.12 | 0.04 | 0.98 | 0.005| 0.01 | -    | Bal.  | 2.7x10^22
|        | Error  | 0.01 | 0.04 | 0.06 | 0.02 | 0.01 | 0.05 | 0.003| 0.005| -    | Bal.  | 1x10^23 |
| KRB-A  | Trepan | 0.11 | 1.07 | 0.39 | 0.24 | 0.11 | 0.52 | 0.072| 0.10 | 0.016| Bal.  | 8.5x10^22
|        | Error  | 0.01 | 0.10 | 0.02 | 0.02 | 0.01 | 0.02 | 0.009| 0.01 | 0.005| Bal.  | 8.5x10^22
| KRB-A  | Test   | 0.09 | 0.88 | 0.29 | 0.20 | 0.14 | 0.57 | 0.052| 0.04 | 0.002| Bal.  | 8.5x10^22
|        | Error  | 0.01 | 0.04 | 0.02 | 0.01 | 0.01 | 0.04 | 0.005| 0.01 | 0.002| Bal.  | 8.5x10^22

---
Table 6.3: Composition of HT-9 alloy (Heat 91345) (from Clausing and co-workers\textsuperscript{(112)})

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
<th>at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.58</td>
<td>0.54</td>
</tr>
<tr>
<td>Cr</td>
<td>12.11</td>
<td>12.81</td>
</tr>
<tr>
<td>Mo</td>
<td>1.03</td>
<td>0.59</td>
</tr>
<tr>
<td>W</td>
<td>0.53</td>
<td>0.16</td>
</tr>
<tr>
<td>Si</td>
<td>0.21</td>
<td>0.41</td>
</tr>
<tr>
<td>Mn</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Al</td>
<td>0.034</td>
<td>0.07</td>
</tr>
<tr>
<td>C</td>
<td>0.21</td>
<td>0.96</td>
</tr>
<tr>
<td>S</td>
<td>0.003</td>
<td>0.01</td>
</tr>
<tr>
<td>P</td>
<td>0.008</td>
<td>0.01</td>
</tr>
<tr>
<td>N</td>
<td>0.004</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>bal.</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Upon removal from the reactor, the samples were prepared for analysis using an Auger Electron Spectrometer. The analysis of the samples consisted of surface examination followed by sputtering to remove atomic layers in order to determine the depth of any segregated layers found. An example of the results obtained from this analysis can be seen in Figure 6.2 for the samples irradiated at 410°C. The concentrations indicated are average values taken from seven areas on three exposed macro-facets.

![Figure 6.2: Concentration versus depth from macro-facets found in samples irradiated at 410°C (from Clausing and co-workers\textsuperscript{(112)})](image)

Observation of the fracture surfaces of the irradiated samples showed that there existed micro- and macro-facets. Micro-facets were assumed related to the underlying lath packet structure of the alloy. Typically, the facets were of the order of 2-5 \(\mu\text{m}\) in size. Analysis of these micro-facets indicated little or no segregation of any alloying elements.

In comparison, macro-facets were found to be between 25 and 50 \(\mu\text{m}\) in size. These macro facets were thought to be due to fracture along different microstructural features than the lath boundaries. However, very few macro-facets were found in samples irradiated at the higher temperatures of 520 and 565°C.

Analysis of those facets found indicated that there was significant enrichment of the elements nickel, chromium, silicon and phosphorus. The enrichments recorded were Chromium \(~1.4\) times, Silicon \(~10\) times and phosphorus \(~100\) times. Nickel exhibited a different behaviour. At the surface, the enrichment factor was found to be \(~8\) times. This
enrichment increased up to a distance of 60nm from the surface, where a figure of ~16 times was observed. At distances of further than 60nm, the enrichment appeared to diminish. This segregation behaviour was in contrast to the macro-facets analysed in the thermally aged material, which showed enrichments of carbon, chromium and molybdenum, indicating the presence of carbides.

Morgan and co-workers\textsuperscript{[113]} together with Faulkner and co-workers\textsuperscript{[114]} examined the segregation of chromium, silicon and nickel in FV448 12CrMoVNb martensitic steel due to irradiation in a fast breeder reactor. The irradiation conditions were 25dpa at 400°C and 46dpa at 465°C. In comparison to typical LWR irradiation conditions, and recalling the discussion regarding neutron energies in Chapter 2, these irradiation doses are far higher than those found in LWR systems.

![Graph showing solute segregation to lath boundaries in FV-448 grade 12%CrMoVNb martensitic steel irradiated at 465°C](from Morgan and co-workers\textsuperscript{[113]})

Following irradiation, the samples were analysed using a VG HB501 FEGSTEM equipped with a windowless EDX detector. Again, recalling earlier discussion, the use of FEGSTEM permits composition profile determination across suitably aligned grain and lath boundaries. Analyses were performed at points on the boundary, and at distances 2.5, 5, 10, 50 and 100 nm from the boundary. Results obtained from the analysis of samples irradiated at 465°C are shown in Figure 6.3. Comparison with the un-irradiated samples indicated that chromium became markedly redistributed, exhibiting a W-shaped profile around the boundary. Both nickel and silicon exhibited highly enriched regions within a few nanometres.
of the boundary, surrounded by a larger region of solute depletion. Of the elements analysed, silicon appeared to be the only element that was sensitive to the irradiation conditions that induced segregation, showing greater segregation at the lower irradiation temperature than the higher temperature.

High-manganese, low-activation martensitic steels have been analysed by Kimura and co-workers\textsuperscript{[115]}. Low activation steels are becoming increasingly important owing to their reduced radioactivity following exposure. Two alloys systems were considered in this work: firstly a 9Cr-1W-2Mn alloy and secondly a 12Cr-1W-6Mn alloy. Other minor additions were carbon, vanadium, silicon, nitrogen, phosphorus and sulphur. Samples were analysed both prior to, and post irradiation using AES. The irradiation conditions were $3 \times 10^{22}n/cm^2$, corresponding to a dose of 10dpa, at a temperature of 638K (365°C). The irradiation of the samples was carried out using the Fast Flux Test Facility Materials Open Test Assembly (FFTF/MOTA), located at the Pacific Northwest Laboratory in the USA.

Prior to irradiation, the samples exhibited transgranular cleavage during fracture. However, post irradiation, the fracture mechanism became that of intergranular cracking. The analyses performed indicated that a different mechanism was occurring in both alloys. In the 9r-1W-2Mn alloy, the results indicated the presence of significant silicon concentrations at the grain boundary. Enrichment of manganese was found at the grain boundaries of the 9r-1W-6Mn alloy. It was assumed that the silicon enrichment at the grain boundaries was causing the carbon at the grain boundaries to be removed (site competition), which in turn caused the embrittlement of the alloys. The manganese enrichment observed was thought to reduce the grain boundary strength, thereby causing embrittlement. It was also thought that the segregation of manganese might promote the formation of $\chi$-phase intergranular precipitates, which may also embrittle the material.

Further discussion of these alloys was presented by Jones and Gelles\textsuperscript{[116]} in relation to the use of such alloys for LWR in-core components. Typically, these alloys had found use in fast breeder-type reactors, owing to their excellent swelling and irradiation-creep resistance. In addition, these alloys exhibit better thermal conductivity, thermal fatigue resistance and corrosion resistance to liquid metals.

The void swelling characteristics have also found favour with the fusion research community, who are currently considering these alloys for use in possible fusion reactor designs. Ferritic/martensitic steels typically require high incubation fluences for the onset of void swelling, and then exhibit low steady state swelling rates. The alloy HT-9, discussed previously, develops less than 1 percent void swelling following irradiation at 420°C to a dose of 110dpa.

The reduced activation of these steels arises due to the removal of certain elements from the alloys that produce long-lived radioactive isotopes. Thus, tungsten stabilised martensitic steels have been developed, typically containing between 7 and 9 percent chromium and up to 2 percent tungsten.
Modified alloys of HT-9 were analysed by Klueh and Alexander in relation to low-fluence embrittlement\textsuperscript{[117]}. In all, three alloys were examined. The alloys were nominally 9Cr-1MoVNb, 12Cr-1MoVW and 12Cr-1MoVW-2Ni. Samples of the alloys were placed in the high-flux isotope reactor (HFIR) and irradiated at 300 and 400°C. The total neutron fluence obtained was $8.4 \times 10^{25} \text{n/m}^2$; the maximum fast fluence ($E > 0.11 \text{MeV}$) was $2.3 \times 10^{25} \text{n/m}^2$ and the maximum thermal fluence was $3.4 \times 10^{25} \text{n/m}^2$. These figures correspond to a maximum damage level of 2.5dpa at the sample capsule mid-plane, decreasing symmetrically with distance to 1.1dpa at the capsule ends.

### 6.2.3 Observations of RIS in stainless steels

As mentioned previously, there has been considerable work investigating the effect of irradiation assisted stress corrosion cracking (IASCC). The phenomenon occurs in austenitic alloys due to the segregation of chromium. During irradiation, it has been observed that chromium will become depleted in the region immediately adjacent to the grain boundaries. This depletion of chromium causes the sensitisation of the grain boundary to corrosive attack. The process is therefore of considerable importance, owing to the widespread use of austenitic stainless steels for in-core reactor components.

Williams and co-workers\textsuperscript{[118]} analysed the irradiation damage that occurs in 12Cr-15Ni-Si austenitic alloys. The interest surrounding this alloy was primarily the void-swelling resistance exhibited by austenitic alloys, together with how it varies with the material composition. In all, four alloys were prepared, with silicon bulk concentrations between 0.14 and 1.42wt.%. Samples were irradiated at a range of temperatures between 400 and 645°C, and at doses between 12.7 and 23.6dpa. Thermal control samples were aged for 13300 hours at the same temperatures in order to isolate any irradiation effects. The samples were analysed using FEGSTEM to provide grain boundary segregation data.

It was found that irradiation caused the microstructure of the alloys to transform from austenite to ferrite in all samples bar the low silicon alloy. This transformation was also seen to follow some form of temperature dependence. At low temperatures, the austenite to ferrite transformation was observed throughout the grains of the samples. However, at higher irradiation temperatures, this transformation was restricted to a region immediately adjacent to the grain boundaries.

In terms of segregation, it was observed that nickel and silicon became enriched at grain boundaries. Chromium, on the other hand, became depleted. Silicon was also observed to accelerate the segregation of the other major alloying elements. Silicon was also assumed to segregate owing to its strong interaction with point defect sinks, whereas the nickel, chromium and iron atoms segregate by enhanced exchange rates with vacancies with the lattice; the Inverse Kirkendall Effect.

The difference in the segregation of the various elements also caused a change in the structure of the material near the grain boundary. The results shown in Figure 6.4
indicate this alteration of structure from b.c.c. to f.c.c. The austenitic structure at the boundary was assumed to be due to the enrichment of nickel, and the corresponding depletion of both chromium and iron. Further away from the boundary, beyond approximately 200nm, the structure became bcc. This corresponds to the enriched concentrations of chromium and iron and the depletion of the nickel.

Figure 6.4: Compositional variation near grain boundary in 12Cr-15Ni-Si irradiated at 645°C (from Williams and co-workers\cite{118})

Watanabe and co-workers\cite{119} have also investigated the radiation induced segregation processes within an austenitic model alloy. The alloy examined was Fe-20Ni-15Cr, with impurities of carbon and nitrogen present in very small quantities (less than 0.003wt.\%). Of interest is the irradiation procedure. The samples were irradiated using 1MeV electrons, using a high-voltage electron microscope. This irradiation caused a damage rate of 5x10^{-4} dpa/s, which is far higher than any irradiations that have been performed using light water and fast breeder type reactors. The temperature range used for the irradiations was between 743 and 803K.

Observations of the irradiated material indicated that migration of grain boundaries occurred, an effect that has not been discussed thus far in the literature discussion. The results indicated that this migration was strongly temperature dependent, together with the orientation of the boundaries. The temperature and dose dependence of the migration can

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure6.4.png}
\caption{Compositional variation near grain boundary in 12Cr-15Ni-Si irradiated at 645°C (from Williams and co-workers\cite{118})}
\end{figure}
be seen in Figure 6.5. Grain boundaries, which were symmetrical, exhibited no migration, whereas those boundaries with a high degree of asymmetry migrated considerably.

![Figure 6.5: Temperature and dose dependence of grain boundary migration observed in Fe-20Ni-15Cr model alloys (from Watanabe and co-workers)](image)

In terms of segregation, it was found that nickel became enriched and chromium depleted at grain boundaries. Moving away from the boundary plane, the nickel then became depleted, whereas the chromium became enriched. Segregation was also observed on those boundaries that had migrated. The boundary migration was thought to be due to the diffusivity of interstitials, as opposed to the diffusivity of vacancies.

6.2.4 Observations of Ris in model alloys

Mahon and co-workers\textsuperscript{[39]} analysed a series of ferritic stainless steels based on an iron-12% chromium binary system, irradiated to 10dpa. The irradiations were performed using two different techniques. The first technique employed used a High Voltage Electron Microscope (HVEM) to bombard the samples with 1 MeV electrons at a dose rate of 2.7x10\textsuperscript{-3} dpa/s. The irradiation was performed for a period of 1 hour at 4 different temperatures, ranging from 350-650°C. The second method was to irradiate the samples by bombarding with 52MeV Cr\textsuperscript{2+} ions in the Variable Energy Cyclotron (VEC), located at Harwell. This would achieve a total dose of 10dpa, at a rate of 2.7x10\textsuperscript{-4} dpa/s at 550°C.

Using a STEM with a probe size of 10nm, analyses across the grain boundary were performed at 10nm intervals. The results indicated that at all temperatures, chromium became depleted at the grain boundaries during irradiation, whereas nickel became enriched. However, the degree of segregation at each temperature varied.

At the lowest irradiation temperature, the profile width is narrow, indicating that the vacancies are essentially immobile. At 450°C, the vacancies are becoming more mobile and
can therefore migrate to the vacancy sinks, taking solute atoms with them. The peak segregation measured occurred at 550°C. However, at 650°C, the profile became much wider, which would indicate that some back diffusion of solute away from the grain boundary is occurring.

The difference in dose rate between the irradiation techniques gave rise to differences in the segregation behaviour exhibited. The lower dose rate of the VEC technique meant that there was less segregation, due to back diffusion of solute atoms.

Attempts were made to measure the segregation of phosphorus in the alloys. It was found that phosphorus became enriched at grain boundaries in the alloy irradiated in the VEC at 550°C. However, since the phosphorus content was low, obtaining a concentration profile across the boundary proved difficult.

The results also indicated that silicon also became enriched at grain boundaries, which would agree with the fact that undersized atoms segregate toward grain boundaries. The oversized elements present in the alloy, namely chromium, molybdenum and vanadium, all became depleted at the boundaries, which would suggest that there exists some inverse Kirkendall or defect-solute binding effect.

Perhaps the most significant model alloy that has been examined both thermally and following irradiation is a Fe-P-C ternary alloy, in work performed by Jones and co-workers\(^{[120]}\). The alloy, containing 30ppm carbon and 1200ppm phosphorus, was examined both in the un-irradiated state, together with following irradiation and thermal ageing. The samples were irradiated under accelerated conditions at 240°C, in the reflector of the Halden heavy-water moderated reactor. The samples, contained within zirconium tubes, were exposed to an average fast neutron dose rate of \(5.4 \times 10^{11}\) dpa/s. Irradiation exposure was between 85 and 251 days. The thermal ageing tests were performed at 240±3°C for 97 and 100 hours. Samples were then examined using SEM, TEM and AES, together with a field emission gun scanning Auger microprobe.

It was found that the behaviour of the intergranular concentrations of phosphorus and carbon was the same in both the aged and irradiated samples. The results obtained are shown in Figure 6.6, together with the corresponding change in the 40J Charpy transition temperature. It can be seen that the phosphorus remains at a constant 0.40 monolayers for all ageing and irradiation times, whereas the carbon falls from 0.44 monolayers in the unirradiated condition towards a stable 0.16 monolayers in the highest dose samples. Nitrogen segregation to grain boundaries was also detected, although no silicon was found.
Figure 6.6: Effect of irradiation or ageing exposure on the shift in 40J Charpy transition temperature and on respective grain boundary monolayer coverages of P and C (from Jones and co-workers[120])

6.3 Theoretical modelling of RIS

As mentioned earlier, radiation induced segregation can be considered a form of non-equilibrium segregation. The effect of the irradiation is to cause a continual flux of defects within the material, and therefore prevent the conditions from attaining equilibrium conditions. The defects created by energetic neutron irradiation are self-interstitial atoms (SIA’s) and vacancies. In modelling the phenomenon, it is necessary to know not only the microstructural parameters of the material but also to have data pertaining to the operational conditions of the system being modelled. Therefore, the irradiation dose and dose rate will need to be determined, together with the operating temperature of the reactor.

Theoretically, the mechanism proposed for radiation-induced segregation to grain boundaries was that of SIA-solute complex formation. These complexes would exist between the SIAs, created by the neutron irradiation, and undersized solute or impurity atoms. Oversized solute atoms, conversely, would be more readily accommodated in substitutional lattice sites and, as such, would migrate away from the vacancy sinks by a vacancy migration mechanism.

As with the modelling work presented for thermal non-equilibrium segregation, there have been many differing attempts to model the phenomenon. Inverse Kirkendall and Rate Theory models have been developed to some success by a range of workers. These models will be briefly highlighted in the following section. However, the analytical approach, originally developed by Faulker and co-workers, will be described in some detail. This model will also be extended to consider segregation of two elements simultaneously. The predictions obtained from this newly extended model will be used to compare with those experimentally observed figures presented in Chapter 4.
6.3.1 Rate Theory and Inverse Kirkendall segregation

Diffusion via Kirkendall effects can be explained quite simply. If an alloy is considered within which elements segregate via solute-vacancy exchange, a concentration of the solute elements across a plane can cause a net flux of vacancies. However, during irradiation, the inverse of this situation occurs. The neutrons irradiating the sample cause the production of point defects; vacancies and SIA’s. The Inverse Kirkendall model of segregation assumes that there are differential solute-vacancy exchange rates between segregating species, which in turn affects their segregation behaviour. Fast diffusing species, such as iron and chromium within an austenitic stainless steel, therefore become depleted at vacancy sinks. Slower diffusing species, which in the cause of austenitic steels is nickel, become enriched at these same vacancy sinks. This process of segregation is shown schematically in Figure 6.7. The segregation profile predicted for the irradiation-induced defects is also shown.

Figure 6.7: Schematic of defect and solute concentration profiles induced by Inverse Kirkendall radiation-induced segregation (from Simonen and Bruemmer[91])

If the fluxes of the segregating elements are considered, this situation can be expressed mathematically. Figure 6.8(a) shows how these mathematically expressed fluxes of vacancies (V) and the elements A and B behave within a binary alloy. The vacancy gradient surrounding the vacancy sink will cause the segregation to the sink of vacancies. Owing to the vacancy-solute exchange mechanism, this process induces a corresponding flux of elements A and B in the reverse direction. Considering the situation where a difference in concentration of elements A and B exists, the flux of the elements will be in proportion to their concentrations. Likewise, any difference in the diffusivities of elements A and B will cause the flux to alter in proportion to the diffusivity. Thus, faster diffusing elements will cause a faster flux of that element away from the vacancy sink.

A similar scenario can be envisaged when considering the flux of interstitials towards interstitial sinks, as shown in Figure 6.8(b). However, owing to interaction
between interstitials and solute atoms, the fluxes of both will be in the same direction. As with the case of the vacancy mechanism, any difference in either solute concentration of diffusivity will correspondingly adjust the flux of the elements towards the sink.

\[ J_A^Y = D_A^Y C_A \quad J_B^X = D_B^X C_B \]

\[ J_A^I = D_A^I C_A \quad J_B^I = D_B^I C_B \]

**Figure 6.8: Schematic of the inverse Kirkendall model of segregation (from Okamoto and Rehn)**

The segregation behaviour of an element is highly dependent upon the flux of point defects towards a sink. Therefore, the point defect production rate, or irradiation dose rate, will therefore govern the segregation that occurs. Additionally, the temperature at which the effect is occurring will also be critical. The relationship between irradiation dose and temperature for the Inverse Kirkendall effect can be shown in **Figure 6.9**. This figure, although based on calculations for dilute alloy systems, has been shown valid for the more concentrated alloy systems, such as the austenitic stainless steels commonly used as structural materials for reactor components. It shows that at faster irradiation dose rates, radiation-induced segregation will only occur at higher temperatures. Below this temperature band, recombination of the point defects will occur; above this temperature and the process of back diffusion will predominate.

**Figure 6.9: Dose rate and temperature dependance of segregation under irradiation (from Okamoto and Rehn)**
In order to model the effect of Inverse Kirkendall segregation, the flux, or rate of flow, of the different segregating species needs to be determined. The modelling approach is therefore often referred to as Rate Theory. As such, Inverse Kirkendall segregation can be determined by Rate Theory. However, Rate Theory can model more than just Inverse Kirkendall type segregation. In some situations, solute atoms interact with the fluxes of interstitials, and migrate as distinct entities. Recalling the discussion pertaining to TNES, the mechanism was assumed to be due to the migration of vacancy-impurity complexes. Under irradiation conditions, not only are vacancies produced by the neutron irradiation, but the formation of self-interstitial atoms (SIA’s) also occurs. Therefore, it is reasonable to assume the interaction between interstitials and impurities, and the formation of mobile SIA-solute atom complexes. The following discussion will briefly highlight the models that have been developed using Rate Theory to predict not only Inverse Kirkendall type segregation, but also segregation arising from the formation of these bound complexes.

6.3.1.1 Modelling dilute alloys systems

The first attempt at utilising Rate Theory models to predict segregation of substitutional impurities in dilute f.c.c. alloy systems was presented by Johnson and Lam\textsuperscript{[122]}. The model incorporated the fluxes of free interstitials, free vacancies, and vacancy-impurity complexes, together with two types (A and B) of interstitial-impurity complexes. Of these interstitial-impurity complexes, type-A complexes were assumed to have long range mobility. Type-B complexes, conversely, could only migrate around the impurity owing to the impurity being caged in a lattice plane, and therefore could not contribute to any grain boundary segregation effects. In their work, theoretical predictions were made for the segregation behaviour of zinc in silver.

![Figure 6.10: Steady-state solute concentration in a 1μm foil irradiated at a rate of 2x10^{-9}dpa/s (from Murphy\textsuperscript{[123]})](image-url)
Since the work just described, there has been considerable work published both utilising and improving the model. Recently, Murphy\cite{122} presented modifications to the dilute alloy Rate Theory model, together with predictions for the segregation of silicon in nickel. The modifications considered were improved parameters for the coupling between solute atoms both vacancies and interstitials. An example of the predictions obtained from the improved model is shown in Figure 6.10. The results presented are the silicon segregation predictions determined at 500 and 550°C, as a function of distance from the grain boundary.

More recently, English and Agnew\cite{124} have modified the models of Murphy and Perks and applied them to phosphorus segregation within a bcc matrix. The model considers the segregation of vacancies, vacancy-phosphorus pairs, interstitials and interstitial-phosphorus pairs, as well as internal sinks for both vacancies and interstitials. The extension of the model has been performed following Molecular Dynamics simulations of interstitial migration processes within the bcc matrix. These simulations returned predictions for the frequency of different mechanism of migration occurring. It was found that of four possible migration mechanisms, three occurred with high frequency. These mechanisms of migration were considered in the subsequent modelling work.

The predictions for the grain boundary segregation of phosphorus in a bcc matrix showed little temperature dependence, up until the effects of thermal segregation become dominant. This can be seen in Figure 6.11, for an alloy with 0.05wt.% phosphorus, irradiated to a dose of 0.002dpa.

![Figure 6.11: Temperature dependence of Rate Theory predictions for phosphorus segregation in a bcc matrix (from English and Agnew\cite{124})](image)

Dose and dose rate were both found to influence the predictions. The dose rate effect can be seen in Figure 6.12 at a temperature of 200°C and a dose of 0.002dpa.
Additional work investigating phosphorus segregation in a Fe-0.4wt.%P model alloy has been performed by Kameda. This work predicted slightly higher grain boundary segregation, although the bulk content of phosphorus was higher.

![Dose rate dependence of Rate Theory predictions for phosphorus segregation in a bcc matrix (from English and Agnew)](image)

**Figure 6.12:** Dose rate dependence of Rate Theory predictions for phosphorus segregation in a bcc matrix (from English and Agnew)

### 6.3.1.2 Modelling concentrated alloy systems

Following the early models for segregation within dilute binary alloys developed by Johnson and Lam\cite{122}, modifications were made by Wiedersich, Okamoto and Lam\cite{125} to predict segregation within a concentrated binary alloy system. The most significant modification to the model was the removal of any flux of vacancy-solute complexes. It was argued that as the concentration of substitutional solute atoms is increased above a few atomic percent, the situation would arise where a single migrating vacancy would be adjacent to more than one nearest neighbour solute atom. The nature of the complex would therefore become more difficult to define, owing to the interactions between one vacancy and more than one solute atom. In a similar vein, interstitial atom jumps simultaneously involving different elements have also been neglected. The simplifications made to the model meant that only a set of three space- and time-dependent coupled partial differential equations needed to be solved. These equations considered the diffusivities of elements A and B within a binary alloy, and their diffusion via interstitials and vacancies. Thus, a flux of irradiation created interstitials drives a flux of elements A and B in the same direction, whereas a flux of vacancies drives the two elements in an opposite direction. More recently, Perks and Murphy\cite{126} have developed a more rigorous theory for diffusion in concentrated alloys, considering what was termed a 'random alloy model'. The model also considered the segregation behaviour of elements in a concentrated ternary alloy system.
As an example of the complexity of the modelling approach, the model of Watanabe and co-workers\cite{119} will be briefly summarised. The model starts by considering the time-dependent behaviour of the segregating species, which can be determined from:

\[
\frac{dC_k}{dt} = -\Omega V \cdot J_k \tag{6.1}
\]

where: \(C_k\) denotes the concentration of the particular segregating species.
\(\Omega\) is the atomic volume.
\(J_k\) is the flux of the particular segregating species.

Since the majority of work developing the model has been based on the segregation characteristics of austenitic stainless steels, \(K\) in equation 6.X can represent the elements iron, chromium or nickel. The time-dependent behaviour of the diffusing vacancies and interstitial point defects are determined from:

\[
\frac{dC_v}{dt} = -\nabla \cdot J_v + \eta K_0 - R C_v C_i - K_i C_s (C_v - C_v^0) \tag{6.2}
\]

\[
\frac{dC_i}{dt} = -\nabla \cdot J_i + \eta K_0 - R C_v C_i - K_i C_s (C_i - C_i^0) \tag{6.3}
\]

where: \(C_v\) is the concentration of vacancies.
\(C_i\) is the concentration of interstitials.
\(J_v\) is the flux of vacancies.
\(J_i\) is the flux of interstitials.
\(C_v^0\) is the bulk equilibrium vacancy concentration.
\(C_i^0\) is the bulk equilibrium interstitial concentration.
\(R\) is the recombination coefficient.
\(\eta\) is the damage efficiency of the electron irradiation, equal to 1.

The fluxes of the three elements \(A, B\) and \(C\) can therefore be written as:

\[
\Omega_A = -D_{A} C A V C_A + d_{A} C_A V C_V - d_{A} C_A V C_i \tag{6.4}
\]

\[
\Omega_B = -D_{B} C B V C_B + d_{B} C_B V C_V - d_{B} C_B V C_i \tag{6.5}
\]

\[
\Omega_C = -D_{C} C C V C_C + d_{C} C_C V C_V - d_{C} C_C V C_i \tag{6.6}
\]

where: \(D_{(A,B,C)}\) represents the diffusivity of element \(A, B\) or \(C\).
\(D_{(A,B,C,V,V)}\) represents the diffusivity of the complex between element \(A, B,\) or \(C\) and either the vacancies or interstitials.

The fluxes of the vacancies and interstitials can be written:

\[
\Omega_i = -(d_{A} - d_{C}) C A V C_A - (d_{B} - d_{C}) C B V C_B - D_i V C_i \tag{6.7}
\]

\[
\Omega_v = -(d_{A} - d_{C}) C A V C_A - (d_{B} - d_{C}) C B V C_B - D_V V C_V \tag{6.8}
\]

where: \(K_0\) is the irradiation damage rate.
α is a thermodynamic factor, equal to 1 (ideal solution condition)

K vs is the internal sink (dislocations and voids) strength (discussed in the following section in relation to analytical models).

The total diffusivities, $D$, and the intrinsic diffusivities, $d$, used in the above equations can therefore be determined from:

$$D_A = d_{AV} C_V + d_{AC} C_I$$  \hspace{1cm} (6.9)  

$$D_V = (d_{AV} + d_{BV} + d_{CV}) C_V$$  \hspace{1cm} (6.10)  

$$d_{ij} = \frac{\bar{Z} \nu_{ji}}{6}$$  \hspace{1cm} (6.11)  

where:  

$\nu_{ji}$ is the defect (j) and solute (k) pair jump frequency, from $\nu_{ji} = \nu_{j}^{0} \exp \left(\frac{-E_{j}^{m}}{kT}\right)$

$\bar{Z}$ is the recombination site number.

$\lambda$ is the unit size as a jump number.

$E_{j}^{m}$ is the migration energy of the defect-solute pair.

The boundary conditions of the equations are firstly that the fluxes of all species are equal to zero deep in the bulk of the material. Secondly, the concentrations of vacancies and interstitials at the grain boundary for the starting condition can be determined from:

$$C_{V}^{0} = \exp \left(\frac{S_{V}^{f}}{k}\right) \exp \left(\frac{-E_{V}}{kT}\right)$$  \hspace{1cm} (6.12)  

$$C_{I}^{0} = \exp \left(\frac{S_{I}^{f}}{k}\right) \exp \left(\frac{-E_{I}}{kT}\right)$$  \hspace{1cm} (6.13)  

where:  

$S_{V,I}^{f}$ and $E_{V,I}^{f}$ are the point defect formation entropy (S) and energy (E).

Although the equations here only outline the basics of the model, it can clearly be seen that the mathematics of the model are complex. The solution of the flux equations is through simultaneous differential equations. In addition, there is no allowance for any microstructural parameters, such as grain size and dislocation density, in the modelling approach. These features are incorporated into the analytical mode, which is presented in the following section.
6.3.2 Analytical approach to modelling

In Chapter 5, an approach to modelling the thermal non-equilibrium segregation of impurity elements was presented. This model assumed that during thermal non-equilibrium conditions, such as during a quench, a concentration gradient of vacancies between the grain centre and the grain boundaries is created. This concentration gradient permits the segregation of vacancies from the grain interior to the grain boundaries. Any impurity atoms that are present in the alloy that preferentially bind to vacancies will therefore be dragged to the grain boundary owing to the formation of vacancy-impurity complex species. The impurity atoms therefore tend to enrich the grain boundary owing to this solute-drag effect.

During irradiation by energetic neutrons, a continual production of point defects occurs within the material. The material can therefore be though of as being in non-equilibrium conditions, since this defect production ceases when the irradiation ceases. The point defects that are created are typically SIA's, i.e., atoms of the matrix material that are removed from their regular lattice location and forced into an interstitial location in the lattice. This damage cascade process has been shown schematically in Figure 2.6, and has been modelled successfully using Monte Carlo techniques by Bacon and co-workers[161].

Within the grain centres of the material, the concentration of these SIA's far exceeds the concentration that is maintained at the grain boundaries. Therefore, a driving force for the migration of SIA's is created during irradiation. It was shown in discussing the modelling of TNES that any interaction between impurity atoms and vacancies permits the formation of vacancy-impurity complexes. In the case of the SIA, if there exists an interaction between any solute impurity atoms and the SIA, the impurity atom will preferentially bind with the SIA to form an SIA-impurity complex. The migration of this species to the grain boundary therefore causes the enrichment of the solute impurity atoms at the grain boundaries.

6.3.2.1 Irradiation enhanced diffusion

During irradiation, the diffusion coefficient of solute atoms will be enhanced, owing to the creation of a continued flux of point defects. This irradiation-enhanced diffusion of solute atoms is a critical parameter in the development of a model to predict irradiation-enhanced segregation. This parameter will therefore be determined prior to the development of the RIS model. The development of the theory for irradiation enhanced solute diffusion presented here diffusion is taken from the work of Nikolaeva and co-workers[184] and Faulkner and co-workers[127].

The diffusion coefficient, $D_v$ of a substitutional solute atom in a matrix is the ability of the atom to migrate through the material. Since substitutional atoms migrate by vacancy-exchange, the concentration of vacancies within the material is therefore critical. Likewise, the energy required for the exchange to occur, and the frequency at which these exchanges...
can occur, are both required to determine the diffusivity. The diffusion coefficient can therefore be expressed as:

\[ D_i = \theta v C_v \exp \left( \frac{-G_M}{kT} \right) \]  

(6.14)

where:  
\( \theta \) is a material constant.  
\( v \) is the vibrational frequency of the solute atom.  
\( C_v \) is the vacancy concentration.  
\( G_M \) is the free energy required for a solute atom to migrate from an equilibrium lattice position to a nearest neighbour site.

In this equation, the only variable is the vacancy concentration. This variable is dependent upon the irradiation dose rate that is creating the additional vacancies over and above the thermal equilibrium concentration. The remainder of the equation is therefore only a function of the irradiation temperature. The equation can be re-written as:

\[ D_i = \delta(t) C_v \]  

(6.15)

where:  
\( \delta(t) \) is a constant, from \( \delta(t) = \theta v \exp \left( \frac{-G_M}{kT} \right) \)

During continued irradiation, the vacancy concentration is therefore equal to the sum of the thermal equilibrium vacancy concentration, \( C^e_v \), and the irradiation-created vacancy concentration, \( C'_v \). This relationship can be expressed as:

\[ C_v = C^e_v + C'_v \]  

(6.16)

where:  
\( C^e_v \) can be determined from \( C^e_v = A_v \exp \left( \frac{-E_{nv}}{kT} \right) \)

The determination of the irradiation-created vacancy concentration, \( C'_v \), is more complex. This concentration is dependent upon the irradiation dose rate, together with the vacancy diffusion coefficient, the vacancy sink strength and the long-range recombination of point defects created during irradiation. The concentration can therefore be expressed as:

\[ C'_v = \frac{BGF(\eta)}{D_v k^2_{\delta v}} \]  

(6.17)

where:  
\( B \) is the dose rate correction factor.  
\( G \) is the irradiation dose rate.  
\( F(\eta) \) can be determined from \( F(\eta) = \frac{2}{\eta} \left[ \sqrt{1 + \eta} - 1 \right] \)

\( D_v \) is the vacancy diffusion coefficient, from \( D_v = D_{ov} \exp \left( \frac{-E_{nv}}{kT} \right) \)
The final parameter listed here, the vacancy sink strength of dislocations, arises due to the interaction that exists between dislocations and point defects within materials. Dislocations create a relaxation of the matrix. This relaxation acts as an attractive force for irradiation created point defects, such as vacancies and interstitial atoms. More detailed discussion pertaining to dislocations as vacancy and interstitial sinks can be found in the work of Bullough and co-workers\textsuperscript{[128,129]} and in the review paper of Matthews and Finnis\textsuperscript{[26]}. The sink strength for vacancies can be determined from:

\[ k_{sv}^2 = Z_v \left( \frac{6}{R} + \sqrt{Z_v \rho} \right) \]  

(6.18)

where:  
- \( Z_v \) is the vacancy bias parameter, equal to 1.  
- \( \rho \) is the temperature dependent dislocation density, from \( \rho = \rho_0 \exp\left(\frac{E_a}{kT}\right) \)  
- \( \rho_0 \) is the prior to irradiation dislocation density.  
- \( E_a \) is the activation energy for dislocation recovery.  
- \( R \) is the material grain size.  

This equation takes into consideration both dislocation density and grain size. However, the effect of the grain size is somewhat 'smeared', as the equation considers uniformity of dislocations throughout the grain.

The function \( F(\eta) \) in Equation (6.17) gives the recombination and thermal emission of the defect population. The \( \eta \) term can be determined from:

\[ \eta = \frac{4\lambda B G}{k_{sv}^2 k_{si}^2 D_v D_i} \]  

(6.19)

where:  
- \( D_i \) is the interstitial diffusion coefficient in the matrix, from \( D_i = D_{oi} \exp\left(\frac{-E_a}{kT}\right) \)  
- \( D_{oi} \) is the pre-exponential constant for the diffusion of interstitials.  
- \( E_a \) is the migration energy for interstitial diffusion.  
- \( k_{si}^2 \) is the interstitial sink strength, from \( k_{si}^2 = Z_i \left( \frac{6}{R} + \sqrt{Z_v \rho} \right) \)  
- \( Z_i \) is the interstitial bias parameter.  
- \( \lambda \) is the long range recombination coefficient of freely migrating point defects, from \( \lambda = \frac{21 D_i}{b^2} \)  
- \( b \) is the interstitial jump distance.
The interstitial bias parameter included in the determination of the sink strength equation differs to that of the vacancy bias parameter. It has been shown that interstitials have a larger relaxation volume than vacancies, which in turn causes a greater flux of interstitials to dislocations than vacancies.

Substituting Equation (6.16) into Equation (6.15) therefore yields the irradiation enhanced solute diffusion coefficient, $D^*_i$, as a function of the thermal and irradiation induced vacancy concentrations:

$$D^*_i = \delta(t)\left(C_s^T + C_v^T\right)$$

(6.20)

Under purely thermal conditions, there are no irradiation-created vacancies. Equation (6.20) can therefore be re-written to express $\delta(t)$ as a function of the thermal diffusion coefficient and the thermal equilibrium concentration of vacancies, both of which are known values. The equation for $\delta(t)$ can therefore be expressed as:

$$\delta(t) = \frac{D^T}{C_S^T}$$

(6.21)

Substituting this equation into Equation (6.20) gives the irradiation enhanced solute diffusion coefficient as:

$$D^*_i = D^T\left(\frac{C_S^T + C_v^T}{C_S^T}\right)$$

(6.22)

This equation relates the irradiation-induced concentration of vacancies to the enhanced diffusion of the substitutional solute atoms. This equation, however, cannot be used for cases where the solute atoms segregating are interstitials. Interstitials do not migrate via vacancy exchange mechanisms, and are therefore unaffected by any irradiation-created vacancies.

6.3.2.2 Complex migration during irradiation

The model developed for TNES in Chapter 5 assumed that the mechanism of solute segregation was the formation of freely migrating vacancy-solute atom bound complexes. These bound complexes could migrate towards grain boundaries and other vacancy sinks owing to the concentration gradient of vacancies adjacent to these sinks set up by the non-equilibrium conditions. The vacancy-solute atom bound complex was shown to occur where the vacancy and solute atom occupied nearest neighbour sites in the lattice. Migration of these complexes was determined to be either dissociation followed by recombination, or through a non-dissociation process, which required a higher energy jump of the vacancy through the lattice.

The mechanism of radiation induced segregation to grain boundaries assumes a similar solute-drag mechanism. However, in this case, the complexes that form are assumed interstitial-solute atom complexes. For ferritic steel alloys, having a body centred cubic lattice...
structure, the most stable configuration for these self interstitial atoms is in the form of a dumbbell orientation, or split interstitial. In this configuration, the split interstitial dumbbell consists of two atoms associated with a single lattice position. The stable alignment of these dumbbells is the <110> orientation, as shown in Figure 6.13(a). Owing to the high strain associated with the formation of these species, the thermal equilibrium concentration is low.

These dumbbells can migrate through the material in a number of ways. Johnson\(^{130}\) performed calculations that demonstrated a two step migration process of the <110> dumbbell, with an intermediate stage of a <223> dumbbell configuration. This process is shown below in Figure 6.13(a) to (c). In this process, one of the SIA’s making the dumbbell configuration moves toward a neighbouring atom. In the example, this movement is toward the body centred atom. This movement forces the atom out of its regular lattice location and into an interstitial location, and the complex becomes formed in the alignment shown in Figure 6.13(b). The remaining SIA from the first dumbbell then returns to its regular lattice location. The process then repeats, with the resulting movement to the orientation shown in Figure 6.13(c).

![Figure 6.13: Two-step SIA dumbbell migration with intermediate <223> orientation (from Johnson\(^{130}\))](image)

An alternative migration process can be seen in Figure 6.14. In this approach, the dumbbell does not rotate through an intermediate orientation. Instead, one of the self-interstitials making the dumbbell in Figure 6.14(a) moves towards its nearest neighbour atom, causing the formation of a new complex shown in Figure 6.14(b).
Austenitic stainless steels, having a face centred cubic lattice structure, will contain stable self-interstitial dumbbells configured in the \langle 100 \rangle orientation. Details of this configuration, and its migration, can be found elsewhere in the literature.

It has been shown that the self-interstitial dumbbell interacts with undersized solute atoms, owing to the strain fields surrounding both species. The result of these interactions is the formation of SIA-solute atom bound complexes. In these complexes, one of the SIA's in the dumbbell configuration is replaced by the undersized solute atom. The complex binding exists due to the undersized solute atom being able to easily locate in the strained lattice surrounding the irradiation-induced SIA. Oversized atoms, on the other hand, tend to remain in substitutional lattice locations, where they segregate away from vacancy-sinks by vacancy exchange mechanisms.

The binding energy of vacancy-solute atom complexes has been covered in detail in the discussion of TNES. Using a similar approach, the binding energy of SIA-solute atom complexes, $E_{ij}$, have been calculated. The binding energy is equal to the sum of the interstitial and impurity formation energies, less the formation energy of the interstitial-solute atom complex, thus:

$$E_{ij} = E_{i} + E_{j} - E_{ij}$$  \hspace{1cm} (6.23)

where: $E_{i}$ is the interstitial atom formation energy.
\( E_i \) is the impurity atom formation energy.
\( E_{ij} \) is the interstitial-impurity complex formation energy.

This equation can be expanded and written in terms of the radii of the interstitial, impurity and matrix, together with the matrix shear modulus and the interfacial energy between a matrix atom and a perfect lattice, thus:

\[
E_{ij} = \frac{8\pi}{3}G \left[ f_0 (r_i - r_0)^2 + r_i (r_0 - r_k)^2 - r_k (r_i - r_k)^2 \right] + 4\pi r_0^2 S_0
\]

where:
- \( r_0 \) is the matrix atom radius.
- \( r_k \) is the bcc interstitial hole radius, from \( r_k = \left( \frac{3a^2}{8} \right) - \left( \frac{(3a^2)^{1/2}}{4} \right) \)
- \( a \) is the lattice parameter.
- \( r_i \) is impurity atom radius.
- \( G \) is the shear modulus of the matrix.
- \( S_0 \) is the interfacial energy per unit area of the interface between a matrix atom and a perfect lattice.

The calculated binding energies determined for a range of elements in a ferritic matrix are shown in Figure 6.15. It can be seen that the binding energies of SIA-undersized solute atom bound complexes shown here differ somewhat to the binding energies of the vacancy-solute complexes shown in Figure 5.20. The difference lies in the size factor of the solute atoms. In the case of the vacancy-impurity complexes, the binding energy of the bound complex can never become negative, since there will always be some size misfit between the vacancy and the solute atom.

However, the binding energy for the SIA-solute atom complex becomes negative for impurity atoms that have a larger atomic radius than the SIA. This fact is of significance when discussing the segregation behaviour of elements, such as chromium. Chromium has a larger atomic radius compared with iron, and therefore its binding energy to interstitials is negative. This has the effect of causing the chromium to segregate in the opposite direction to the self-interstitials, thereby causing grain boundary to become depleted.
Figure 6.15: Interstitial-impurity atom bound complex binding energies as a function of atomic radius in a ferritic matrix (from Faulkner and co-workers[89])

Phosphorus, on the other hand, is considerably smaller than iron, and therefore has a positive binding energy. The phosphorus atoms therefore preferentially bind with the SIA’s, creating the bound complexes. These complexes will then migrate towards the grain boundary owing to the interstitial concentration gradient that exists between the grain interior and interstitial sink. The sink that is considered of most relevance is the grain boundary, owing to the effect that phosphorus has on its cohesiveness.

The migration of these SIA-undersized solute atom bound complexes is different that that of the SIA dumbbells described previously. In the case of the SIA dumbbell, the atoms that made up the dumbbell were identical to the matrix material. The migration mechanism was due to lattice atoms being forced into interstitial locations. The long-range migration of SIA-undersized solute atom complexes, however, requires that the solute atom to remain within the complex. Four possible mechanisms for migration are shown in Figure 6.16. Only short-range migration is possible by the method shown in Figure 6.16(a), since the undersized solute atom remains ‘caged’ on one plane of the lattice. However, long range migration of the bound complex is possible by the other mechanisms shown in Figures 6.16(b) to (d).
6.3.2.3 Binary modelling of RIS

Having considered the effect of irradiation on solute diffusion coefficients, together with the binding and migration of interstitial-solute atom bound complexes, it is now possible to develop a model to predict radiation induced segregation in both binary and ternary alloys. The first model presented here is a model to predict the radiation-induced segregation of one element within a binary system. This is the simplest approach to modelling the mechanism. This model will then be developed and extended to give predictions for the segregation of an impurity element in a ternary system, where the other element is in competition with the impurity element for grain boundary sites. This is termed the site competition model.

The model developed here is based on the thermal non-equilibrium segregation model of Faulkner\(^{83}\) described in Chapter 5. This model has since been modified and extended to incorporate radiation effects by a range of workers\(^{90,114,132,133}\). The model adopts an analytical approach, and incorporates microstructural features such as dislocation density and grain size.

The first stage of the model is to determine the maximum possible RIS of a solute element. This can be calculated from the driving force for segregation of the SIA-solute atom

---

Figure 6.16: Migration of \(<110>\) SIA-undersized solute atom bound complexes through bcc lattice (from Robrock\(^{131}\))
complexes. The concentration of impurity-point defect complexes, \( C_c \), can thus be determined from:

\[
C_c = k_c C_g C_p \exp\left(\frac{E_{ip}}{kT}\right)
\]

(6.25)

where: 
- \( k_c \) is a geometrical constant.
- \( C_g \) is the solute concentration.
- \( E_{ip} \) is the phosphorus-SIA binding energy.

The point defect concentration, \( C_d \), can be determined from:

\[
C_d = A_t \exp\left(-\frac{E_f}{kT}\right)
\]

(6.26)

where: 
- \( A_t \) is a constant related to the vibrational entropy of atoms around an interstitial.
- \( E_f \) is the interstitial formation energy.

Thus, the ratio of the complex concentration, \( C_c \), to the impurity concentration, \( C_g \), at the grain boundary can be expressed as:

\[
\left(\frac{C_c}{C_g}\right)_{GB} = k_c A_t \exp\left(\frac{E_{ip} - E_f}{kT}\right)
\]

(6.27)

During irradiation, however, the concentration of defects within the grain is continually in a state of change, since the neutron bombardment is causing further defects to be produced. Thus, the point defect concentration needs to be adjusted to allow for this defect production rate. Therefore:

\[
C_d = A_t \exp\left(-\frac{E_f}{kT}\right) + \frac{BG}{D_j k_d^2}
\]

(6.28)

The ratio of the complex concentration to the impurity concentration, \( C_c \), within the matrix of the grains can be expressed as:

\[
\left(\frac{C_c}{C_g}\right)_{m} = k_c A_t \exp\left(\frac{E_{ip} - E_f}{kT}\right) + \frac{k_c BG}{D_j k_d^2} \exp\left(\frac{E_{ip}}{kT}\right)
\]

(6.29)

If the ratio of the matrix concentration to the grain boundary concentration is now calculated, the following expression can be determined:

\[
\left(\frac{C_c}{C_g}\right)_{GB} = 1 + \frac{BG}{A_t D_j k_d^2} \exp\left(\frac{E_f}{kT}\right)
\]

(6.30)

Equation (6.28) can be incorporated with previous work from Faulkner\(^{[81]}\) to account for the absolute concentration of the complexes. This is simply determined by incorporating the ratio of the complex binding energy to the interstitial formation energy. This new
equation also includes the effects of long-range recombination of point defects, which has been discussed in relation to irradiation-enhanced diffusion.

\[
\frac{C^p_{\text{max}}}{C^p_0} = \frac{E_p}{E_f} \left[ 1 + \frac{BGF(\eta)}{A_0 D_1 kT} \exp \left( \frac{E_f}{kT} \right) \right]^{C^p_0 E_i} \frac{C^p_{\text{max}}}{kT} (6.31)
\]

where: \(C^p_0\) is the bulk phosphorus content.

Faulkner and co-workers\(^{[133]}\) modified the TNES model to demonstrate the radiation-induced segregation of silicon in ferritic steels. The modifications included a more rigorous solution to the diffusion equation, incorporating the effect of the grain boundary width, as well as modifying the dislocation density to allow for variations with temperature. The equation to determine the concentration profile adjacent to a grain boundary can be expressed as:

\[
\frac{C - C_0}{C_b - C_0} = 1 - \exp \left( \frac{4D_1 t}{\alpha^2 w^2} \right) \text{erfc} \left( \frac{2\sqrt{D_1 t}}{\alpha w} \right) (6.32)
\]

where: 
- \(C\) is the boundary concentration.
- \(C_0\) is the bulk concentration of solute in the material.
- \(C_b\) is the maximum solute concentration expected at the grain boundary.
- \(D_1\) is the impurity element diffusion coefficient.
- \(t\) is the total irradiation time\(^1\).
- \(\alpha\) is equal to \(C_b/C_0\).
- \(w\) is the grain boundary width.

As with the modelling of TNES presented in Chapter 5, a critical time for desegregation is required for kinetically modelling the mechanism. In the case of TNES, the critical desegregation time was related to the diffusivities of both the vacancy-solute atom complexes and the solute atom. Since the mechanism for RIS is assumed to be the migration of SIA-undersized solute atom complexes, it is this diffusivity that is used. The equation can therefore be expressed as:

\[
t_c = \frac{\alpha^2 \ln(D_C/D_1)}{4(D_C - D_1)} (6.33)
\]

For irradiation times that exceed this critical time, the flux of interstitial-solute atom complexes towards the grain boundary is equalled by the back-diffusion of solute atoms away from the boundary. The concentration at the boundary therefore remains constant after this time.

---

1 The total irradiation time can be determined from dividing the irradiation dose by the irradiation dose rate, resulting in the total irradiation time in terms of seconds.
6.3.2.4 Ternary modelling of RIS

The approach discussed until now only predicts the radiation-induced segregation of elements in a purely binary system. As we have seen from discussion of the materials commonly used for reactor applications, a binary model is clearly inappropriate. This model has therefore been extended to predict the behaviour of two impurity elements within an iron matrix. From the literature that is available, it is apparent that there exists some degree of interaction between various segregating species. Thus, it has been necessary to consider these effects when modelling ternary alloy systems.

The mechanism of radiation-induced segregation in a binary alloy has been assumed that of SIA-solute atom complex diffusion. Thus, one possible approach to model the segregation of two impurity elements within an iron matrix would be to introduce a co-segregation effect to the complex migration process. However, there is no data that would support this mechanism. In order to build in a co-segregation effect, a new mechanism of segregation would be required.

Thus, a site-competition approach has been developed. This approach avoids the requirement to develop a new segregation mechanism. Instead, it assumes that impurity elements are free to segregate towards grain boundaries independently. Once at the grain boundary, however, the atoms of each impurity element compete for the available locations. The main assumption here is that the grain boundary has a structure that allows elements to move freely. Typically, grain boundaries have been assumed totally random structures, and this assumption has been used in modelling the effect.

An additional assumption has been made regarding the maximum possible segregation of the impurity elements. It has been assumed that each element segregates to the grain boundaries independently. However, owing to the neutron irradiation, there is only a finite number of interstitial atoms present within the matrix. Thus, the segregating impurity elements need to compete for these interstitial atoms in order to form the mobile mixed dumbbell complex, which can then segregate to the grain boundary. Therefore, the maximum possible concentration of impurity that could segregate is dependent upon how the two elements compete for the available interstitials.

\[
C_{\text{g}}^{\text{max}} = C_{\text{g}}^p \left( \frac{C_{\text{g}}^p \exp \left( \frac{E_{\text{g}}^p}{kT} \right)}{C_{\text{g}}^c \exp \left( \frac{E_{\text{g}}^c}{kT} \right) + C_{\text{g}}^p \exp \left( \frac{E_{\text{g}}^p}{kT} \right)} \right) \left[ 1 + \frac{BGF(q)}{A_1D_1kT} \exp \left( \frac{E_{\text{g}}^p}{kT} \right) \right] \quad (6.34)
\]

The equation given above relates the maximum possible segregation of an impurity element to a number of factors. However, neither segregating element will reach its maximum grain boundary concentration owing both to the kinetics of segregation, and to the competition for the available grain boundary locations. Therefore, a kinetic expression needs...
to be obtained to incorporate diffusion effects into the model. This expression can be expressed as:

\[
\frac{C_b^0(t) - C_b^g}{C_b^{\text{max}} - C_b^g} = 1 - \exp \left( \frac{4D_P^C t}{\alpha^2 d^2} \right) \text{erfc} \left( \frac{2\sqrt{D_P^C t}}{\alpha d} \right)
\]  

(6.35)

where:  
- \(d\) is the width of the grain boundary.  
- \(D_P^C\) is the diffusion coefficient of Phosphorus-interstitial complexes.  
- \(t\) is the irradiation time.  
- \(C_l\) is the ratio of the maximum predicted radiation induced Phosphorus segregation to the matrix concentration of Phosphorus, from \(C_P^{\text{max}} / C_b^g\).

This kinetic expression determines the level of segregation of each impurity element assuming independent segregation to the grain boundary. Once at the grain boundary, these elements are assumed to be in competition for the available sites. This competition between the elements can be related to their grain boundary binding energies. Likewise, the absolute concentration of each element that is present within the alloy system needs to be considered. Considering these assumptions, a final equation can be written to determine the segregated concentration of each of the impurity elements, as shown in Equation (6.34).

\[
C_b^{\text{p}*} = C_b^0 \left( \frac{C_{\text{p}} \exp \left( \frac{Q_{\text{p}}}{kT} \right) \exp \left( \frac{Q_{\text{c}}}{kT} \right)}{C_b^0 \exp \left( \frac{Q_{\text{p}}}{kT} \right) + C_b^0 \exp \left( \frac{Q_{\text{c}}}{kT} \right)} \right)
\]  

(6.36)

where:  
- \(Q_{\text{p}}\) is the grain boundary binding energy of phosphorus.  
- \(Q_{\text{c}}\) is the grain boundary binding energy of carbon.

It can be seen from the equation that increasing the concentration of either element will reduce the predicted grain boundary concentration of the other element. This would appear to be entirely logical. Likewise, an impurity element with a high grain boundary binding energy will reject an element with a lower binding energy in proportion to the energies of each element.

As with the modelling approach discussed for binary alloys, a critical time is incorporated into the model developed here. The equation for the critical time is the same as that used previously.

6.3.2.5 Ternary modelling of irradiation-enhanced equilibrium segregation

In an approach similar to that of Seah and McLean, the prediction of segregation incorporating site competition has been determined. The maximum predicted phosphorus grain boundary segregation can be determined from:
Allowing for the kinetics of the process, and incorporating irradiation-enhanced diffusion into the calculations, the grain boundary concentration at a time \( t \) can be determined from:

\[
\frac{C_b(t) - C_b^p}{C_b^{max} - C_b^p} = 1 - \exp \left( \frac{4D_c^p t}{\alpha^2 d^2} \right) \operatorname{erfc} \left( \frac{2\sqrt{D_c^p t}}{\alpha d} \right)
\]  

### 6.3.3 Model Parameters

The modelling approaches developed here for predicting RIS in both binary and ternary alloy systems require a number of parameters. These parameters can be categorised as material specific and element specific. Material specific parameters include such things as solute element concentrations, grain sizes and dislocation density. The particular elements that are being modelled will also require a number of parameters, which are independent of the material. The parameters are tabulated in Tables 6.4 to 6.6. Additionally, the irradiation conditions of dose and dose rate are required. The references used to obtain the parameters are shown.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Migration energy for diffusion of interstitials, ( E_m ) (eV)</td>
<td>0.3 [134]</td>
</tr>
<tr>
<td>Pre-exp. constant for diffusion of interstitials, ( D_m ) (m²/s)</td>
<td>5.0 \times 10^{-6}</td>
</tr>
<tr>
<td>Migration energy for vacancy diffusion, ( E_v ) (eV)</td>
<td>1.0 [104] to 1.24 [135]</td>
</tr>
<tr>
<td>Pre-exp. constant for vacancy diffusion, ( D_v ) (m²/s)</td>
<td>5.0 \times 10^{-5} [94]</td>
</tr>
<tr>
<td>Vacancy formation energy, ( E_f ) (eV)</td>
<td>1.4 [94] to 1.6 [104]</td>
</tr>
<tr>
<td>Interstitial atom formation energy, ( E_i ) (eV)</td>
<td>3.0 [136]</td>
</tr>
<tr>
<td>Activation energy for dislocation recovery, ( E_d ) (eV)</td>
<td>0.1 [133]</td>
</tr>
<tr>
<td>Interstitial Bias, ( Z_i )</td>
<td>1.1 [129]</td>
</tr>
<tr>
<td>Grain boundary width, ( d ) (m)</td>
<td>1.0 \times 10^{-9}</td>
</tr>
<tr>
<td>Interstitial Jump distance, ( b ) (m)</td>
<td>1.43 \times 10^{-10} [137]</td>
</tr>
<tr>
<td>Vibrational entropy of atoms around interstitial, ( A_i )</td>
<td>1.0 [138]</td>
</tr>
<tr>
<td>Vibrational entropy of atoms around vacancy, ( A_v )</td>
<td>1.0 [104]</td>
</tr>
<tr>
<td>Numerical constant for critical time calculation, ( \delta )</td>
<td>0.05 [81]</td>
</tr>
<tr>
<td>Dose rate correction factor, ( B )</td>
<td>0.05</td>
</tr>
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</table>

Table 6.4: Material specific parameters used in modelling
### Table 6.5: Phosphorus parameters used in modelling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Activation energy for solute diffusion, $E_a$ (eV)</td>
<td>$2.68$ [139]</td>
</tr>
<tr>
<td>Pre-exp. constant for solute diffusion, $D_{o1}$ (m$^2$/s)</td>
<td>$7.12\times10^{-3}$ [139]</td>
</tr>
<tr>
<td>Solute-interstitial (S-I) complex binding energy, $E_b$ (eV)</td>
<td>$0.57$ [89]</td>
</tr>
<tr>
<td>Migration energy for diffusion of S-I complexes, $E_{mc}$ (eV)</td>
<td>$0.87$ [139]</td>
</tr>
<tr>
<td>Pre-exp. constant for diffusion of S-I complexes, $D_{oc}$ (m$^2$/s)</td>
<td>$8.0\times10^{-7}$ [122]</td>
</tr>
<tr>
<td>Equilibrium segregation energy, $Q$ (eV)</td>
<td>$0.54$ [55]</td>
</tr>
</tbody>
</table>

### Table 6.6: Carbon parameters used in modelling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy for solute diffusion, $E_a$ (eV)</td>
<td>$0.83$ [93]</td>
</tr>
<tr>
<td>Pre-exp. constant for solute diffusion, $D_{o1}$ (m$^2$/s)</td>
<td>$3.94\times10^{-7}$ [93]</td>
</tr>
<tr>
<td>Solute-interstitial (S-I) complex binding energy, $E_b$ (eV)</td>
<td>$1.12$</td>
</tr>
<tr>
<td>Migration energy for diffusion of S-I complexes, $E_{mc}$ (eV)</td>
<td>$1.42$ [139]</td>
</tr>
<tr>
<td>Pre-exp. constant for diffusion of S-I complexes, $D_{oc}$ (m$^2$/s)</td>
<td>$8.0\times10^{-7}$ [122]</td>
</tr>
<tr>
<td>Equilibrium segregation energy, $Q$ (eV)</td>
<td>$0.829$ [44]</td>
</tr>
</tbody>
</table>

### 6.4 Theoretical predictions of RIS

Predictions obtained from the models discussed will now be presented. However, the effect of radiation on the solute diffusion coefficient will first be highlighted. Recalling the discussion in Section 6.3.2.1, radiation will create additional vacancies within the material, which in turn will affect the rate at which the substitutional solute atoms, such as phosphorus, can diffuse through the material. Predictions for this diffusion change will be given for a range of irradiation and material conditions. Following these predictions, the results from both the binary and ternary RIS models will be presented which will incorporate the irradiation enhanced diffusion effect. Predictions from these models will be obtained for sensitivity to a range of material conditions.

#### 6.4.1 Irradiation enhanced diffusion of phosphorus

A comparison between thermal diffusion coefficient and irradiation-enhanced diffusion coefficient of phosphorus is shown in Figure 6.17. The material parameters used for the irradiation enhanced diffusion predictions were:

- Pre-irradiation dislocation density = $1\times10^{14}$ m$^{-2}$
- Grain size = 20 microns
- Dose rate = $1\times10^8$ dpa/s

It can be seen that the enhancement of the diffusion coefficient is at temperatures less than 700K (≈425°C). Recalling the discussion presented in Chapter 2, this effect is of considerable importance to reactor materials by virtue of the fact that many reactor systems operate at temperatures of approximately 300°C.
Figure 6.17: Thermal and irradiation enhanced phosphorus diffusion coefficients as a function of temperature

The enhancement of diffusion coefficients of substitutional phosphorus atoms can also be equated to the irradiation dose rate. Figure 6.18 shows how the diffusion coefficient of phosphorus changes as a function of dose rate. The dose rates selected are representative of those found in light water reactor systems. Again, at lower temperatures, the effect of irradiation enhancement is noticeable, with the diffusion coefficient increasing by two orders of magnitude.

Figure 6.18: Effect of dose rate on the irradiation enhanced diffusion coefficient of phosphorus
Figure 6.19: Effect of dislocation density on the irradiation enhanced diffusion coefficient of phosphorus

The effect of dislocation densities on the diffusion enhancement is shown in Figure 6.19. At higher dislocation densities, irradiation enhanced diffusion of phosphorus is predicted to fall at lower temperatures. At 300°C (573K), there is a difference of 4 orders of magnitude between the dislocation densities of $10^{-12}$ m$^{-2}$ and $10^{-16}$ m$^{-2}$.

6.4.2 Binary alloy predictions

The predictions presented in following figures are obtained from the binary RIS model. Figure 6.20 shows the predictions of RIS and ES for alloy SG. The irradiation conditions selected for these predictions are those for sample SG02, which has experienced both intermediate dose and dose rate in comparison to the other samples of alloy SG. The predictions of RIS are using the data for both interstitial-solute complex migration and vacancy-solute complex migration. The effects due to these mechanisms both appear to diminish at temperatures greater than 350°C. At lower temperatures, below 300°C, the interstitial-solute complex mechanism is more dominant than the vacancy-solute mechanism. Above approximately 420°C, it can be seen that segregation due to equilibrium mechanisms dominates. The figure also shows the experimentally observed segregation obtained from analysis of the samples. The temperature of this irradiation was 255°C. It can be seen that both the SIA-solute atom complex and vacancy-solute atom complex mechanisms greatly over-predict the observed segregation.
Figure 6.20: Segregation predictions for Alloy SG (P=0.043%, dose=12.34mdpa, dose rate = 6.4x10^{-10}dpa/s, grain size = 50\mu m, \rho_0 = 4.2x10^{14}m^{-2})

The effect of grain size on the predictions obtained using the binary RIS model can be seen in Figure 6.21. Again, these predictions have been performed using the data for alloy SG, and the irradiation conditions are quoted. It can be seen that larger grain sizes dramatically increase the predicted RIS, assuming segregation occurs by the SIA-solute atom complex mechanism. This is easily explained, since the increased size of the grains will permit a larger amount of solute to migrate to the grain boundary. Examination of the sink strength equations for interstitials and vacancies indicates that larger grain sizes reduce the sink strength, which in turn increases the point defect concentration created by the irradiation. This therefore creates a larger concentration difference between the grain interior and the grain boundary, thus increasing the driving force for interstitial-solute complex migration.

The effect of varying the prior-to-irradiation dislocation density on the predicted RIS from the binary model is shown in Figure 6.22. The range of dislocation densities used in the predictions was between $10^{12}$ and $10^{15}m^{-2}$. This gives a spread of two orders of magnitude around the actual dislocation density of the material. It can be seen that the low-temperature behaviour of the predictions shows some slight variation. This can be attributed to the effect of the dislocation densities on the phosphorus diffusion coefficient. However, the major difference between the predictions occurs at higher temperatures. As the dislocation density increases, the magnitude of RIS begins to fall at lower temperatures. This is due to the sink efficiency of the higher dislocation densities.
Figure 6.21: Effect of grain size on RIS predictions for Alloy SG (P=0.043%, dose = 12.34x10^{-3} dpa, dose rate = 6.4x10^{-10} dpa/s, $\rho_0 = 4.2x10^{14} m^{-2}$)

Figure 6.22: Effect of dislocation density on RIS predictions for Alloy SG (P=0.043 at.%, dose = 12.34x10^{-3} dpa, dose rate = 6.4x10^{-10} dpa/s)
Figure 6.23: Effect of dose rate on binary RIS predictions for Alloy SG

The effect of the irradiation conditions on the predicted segregation of phosphorus is shown in Figures 6.23 and 6.24. It can be seen from Figure 6.23 that increasing dose rates cause the maximum segregation to remain at higher temperatures. Thus, for a dose rate of $1 \times 10^{12} \text{dpa/s}$, the predicted segregation will fall dramatically over $275^\circ\text{C}$. However, increasing the dose rate up to $1 \times 10^{10} \text{dpa/s}$ raises this drop-off temperature to around $375^\circ\text{C}$.

The effect of irradiation dose can be seen in Figure 6.24. This has a less obvious effect. Although there is some low temperature influence on the results, the most noticeable effects are at higher temperatures. At these temperatures, irradiation-enhanced equilibrium segregation is occurring. Increase the dose causes the irradiation time to increase, assuming a constant dose rate. Therefore, higher doses are caused by longer irradiation times, which permits more equilibrium segregation to occur.
6.4.3 Ternary alloy predictions

The following four graphs (Figures 6.25 to 6.28) show the sensitivity of the ternary model to variations in the prior-to-irradiation dislocation density, irradiation conditions of dose and dose rate and material grain size. The predictions were based on Alloy SG, which was used for comparison of the binary predictions presented earlier. It can be seen that the dislocation density has a similar effect in the ternary model as it does in the binary model. Figure 6.25 shows that as the dislocation density increases, the temperature at which the segregation begins to drop-off is lowered. For a dislocation density of $10^{12}$ m$^{-2}$, the peak segregation occurs at approximately 300°C. However, increasing this figure to $10^{16}$ m$^{-2}$ lowers this temperature to approximately 200°C.
The effect of the irradiation dose rate on the ternary predictions is shown in Figure 6.26. It can be seen that increasing dose rate causes the peak radiation induced segregation to increase, in addition to increasing the temperature at which this occurs. This effect is similar to that predicted by the binary model.
The irradiation dose effect is considered in Figure 6.27. It can be seen that the peak segregation does not vary with changing dose. However, the higher temperature segregation, due to irradiation enhanced equilibrium segregation, does alter. This can be explained by the fact that the irradiation time, which governs the equilibrium segregation behaviour, is altered by changing the dose, since the dose rate for the predictions remained constant. This feature is also shown in Figure 6.26.

Figure 6.27: Effect of dose on ternary model predictions

Figure 6.28: Effect of grain size on ternary model predictions
The grain size effect observed in the predictions obtained from the binary model indicated that larger grain sizes caused the magnitude of radiation induced segregation to increase. This is also observed in the predictions obtained from the ternary model, shown in Figure 6.28. It can also be seen that the grain size of the material has no effect on the higher temperature segregation behaviour which is controlled by irradiation enhanced equilibrium segregation.

The predictions shown in Figures 6.29 to 6.33 plot grain boundary enrichment versus temperature for the exact material parameters and irradiation conditions of the alloys being considered. These predictions assume that the phosphorus content of the material at the start of the irradiation is equal to the bulk figure. The predictions compare the binary model to the newly modified ternary model. The experimental observations of segregation are plotted on each graph for comparison. The data points are those obtained from the work performed at Harwell, presented previously in Chapter 4. The effect of radiation can be obtained by subtracting the mean post-weld heat treated segregation data, shown in Table 4.4, from the post-irradiation condition of the material, shown in Table 4.11. The ternary model predictions were performed for two carbon concentrations. The nominal carbon concentration of each alloy is plotted. However, this concentration will be higher than the carbon that is actually in solution in the material. A lower carbon concentration is therefore plotted for each alloy. The carbon concentration of this alternative prediction has been simply determined by assuming that there is 10 percent of the nominal carbon content in solution.

Figure 6.29: Predictions for alloy SG02 (dose = 12.34 mdpa, dose rate = 6.4x10^-10 dpa/s, ρ = 4.2x10^{14} m^{-2})
Figure 6.30: Predictions for alloy SG25 (dose = 1.5 mdpa, dose rate = $8.9 \times 10^{11}$\ dpa/s, $\rho = 4.2 \times 10^{14}$\ m$^{-2}$)

Figure 6.31: Predictions for alloy SG35 (dose = 29 mdpa, dose rate = $6 \times 10^9$\ dpa/s, $\rho = 4.2 \times 10^{14}$\ m$^{-2}$)
Figure 6.32: Predictions for alloy SP65 (dose = 38 mdpa, dose rate = \(6 \times 10^{-9}\) dpa/s, \(\rho = 3.16 \times 10^{14}\) m\(^{-2}\))

Figure 6.33: Predictions for alloy SL152 (dose = 26.62 mdpa, dose rate = \(6.3 \times 10^{-9}\) dpa/s, \(\rho = 1.5 \times 10^{14}\) m\(^{-2}\))
6.5 Chapter summary

This Chapter has discussed previously adopted modelling approaches to predicting grain boundary segregation. The predictions that these models return have been presented, and can be seen to generally overpredict the experimentally observed segregation. An extended approach to modelling radiation induced segregation has been introduced. This new approach considers the segregation behaviour of ternary alloys. Within the model, there is allowance for grain boundary site competition to occur between the two segregating elements. This extended model would appear to be more applicable to RPV steels, since there are no cases where a pure binary system is used. Predictions obtained from the extended model demonstrate that the overprediction of the binary model is eliminated due to the consideration of a second segregating element. The model also considers the alloy composition, and altering the concentrations of the segregating elements can be seen to have a noticeable effect on the predictions obtained.
Chapter 7: Grain Boundary Precipitation

7.1 Introduction

In Chapter 2, a range of thermally- and irradiation- induced phenomena were discussed. It was shown that thermally induced phenomena generally arise from the increased energy that is available to point defects to migrate and diffuse through the alloy system. Conversely, irradiation-induced phenomena were associated with the microstructural damage that occurs due to the effects of the energetic neutrons that arise from nuclear fission. These damage cascades in turn provided an additional source of mobile point defects to the material, which in turn could migrate and diffuse at a greater rate than in un-irradiated material.

In this Chapter, the broad area of precipitation will be introduced and discussed in some detail. Within the scope of this Thesis, an investigation has been performed into adapting an aluminium-based thermally-induced precipitation model to obtain predictions for similar behaviour in steel alloys. The model predictions have been extended to tens of years, which is of the same order of magnitude as the expected life of many power stations. The material that has been modelled is an austenitic stainless steel, which is a material that is commonly used in power generating applications. Although the material is significantly different to that for which the segregation models have been tailored, the development of such a long-term model is still a useful investigation.

Precipitation, both thermally-induced and irradiation-enhanced, is not generally thought of as a damaging phenomenon. Indeed, many alloy systems are strengthened due to precipitate formation, both along grain boundaries and within the matrix of the grain structure. For example, many aluminium-copper alloys are hardened due to precipitate formation, which effectively impedes the motion of dislocations within the alloy.

Precipitates can be formed either as coherent or as incoherent structures. Incoherent precipitates typically form when a material is slowly cooled from a heat treatment temperature. The lattice structure of these precipitates is different to that of the matrix material, and there is therefore a distinct boundary between the precipitate and the matrix.

Coherent precipitates typically form in materials that have been rapidly cooled to form a supersaturated solution of atoms in the matrix. During ageing processes, the atoms will possess sufficient energy to be able to diffuse through the matrix material and form precipitates. Coherent precipitates have the same lattice structure as the matrix material, and are generally smaller than incoherent precipitates. These coherent precipitates then begin to break bonds with the surrounding matrix material, until there becomes a clear boundary between the precipitate and the matrix and an incoherent precipitate exists. These four stages of precipitate behaviour are shown schematically in Figure 7.1.
It has been shown that irradiation of materials with energetic neutrons will cause the diffusivities of some alloying elements to increase. Chapter 6 highlighted this irradiation enhanced diffusion effect in relation to the segregation of solute atoms to grain boundaries. However, should certain diffusing elements assist in the formation of precipitates, then irradiation would be expected to cause the rate of precipitate nucleation and growth to increase. The phenomenon therefore is of importance when dealing with materials that are candidates for use in nuclear reactor systems.

### 7.1.1 Austenitic stainless steels

The bulk of the work contained in this thesis is based on the behaviour of ferritic RPV steels, in particular, the alloy ASME A533B. The modelling work presented in this Chapter has been based on precipitation within austenitic stainless steel alloy systems. A brief description of this alloy system will be presented highlighting the main features of this alloy and its importance as a structural material in many power-generating applications.

The basis for the development of stainless steel lies in the iron-carbon phase diagram. It is possible to alter the shape and size of the γ-field of the iron-carbon binary phase diagram by additions of certain alloying elements. Additions of nickel and manganese extend this field. Chromium, conversely, makes the γ-field smaller, since the formation of ferrite becomes more favourable.
However, if chromium is added to an iron-carbon alloy containing nickel, it is possible to alter the shape of the $\gamma$-field so that austenite is preserved at room temperatures. A ternary iron-chromium-nickel phase diagram is shown in Figure 7.2. Additions of chromium to the alloy cause the corrosion resistance properties to improve. The chromium promotes the formation of a stable $\text{Cr}_2\text{O}_3$ oxide film on the surface of the alloy. This film remains present to high temperatures, which is why these alloys are commonly used for applications requiring high temperature oxidation and corrosion resistance.

The influence of a range of alloying elements on the structure of chromium-nickel stainless steels can be determined using a Schaeffler diagram, shown in Figure 7.3. This diagram shows the composition of stainless steel at room temperature using axes of chromium and nickel equivalents. These equivalents have been determined empirically, and are expressed as:

\[
\text{Cr}_{\text{eq}} = \text{Cr} + 2\text{Si} + 1.5\text{Mo} + 5\text{V} + 5.5\text{Al} + 1.75\text{Nb} + 1.5\text{Ti} + 0.75\text{W} \quad (7.1)
\]

\[
\text{Ni}_{\text{eq}} = \text{Ni} + \text{Co} + 0.5\text{Mn} + 0.3\text{Cu} + 25\text{N} + 30\text{C} \quad (7.2)
\]
Additions of carbon to Fe-Cr-Ni alloys promote the formation of carbides within the material. There are three main carbide phases that form. These phases are as follows:

(i) Orthorhombic cementite (Fe/Cr)$_3$C which may contain up to 15%Cr
(ii) Trigonal (Cr/Fe)$_7$C$_3$ which contains a minimum of 36%Cr
(iii) Cubic (CrFe)$_2$C$_6$ which contains a minimum of 70%Cr

These phases are formed during annealing of the material, and are dissolved when the material is heated to temperatures over 1000°C.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal structure</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_{79}$C$_6$</td>
<td>D8$_4$</td>
<td>6.97</td>
</tr>
<tr>
<td>Cr$_7$C$_3$</td>
<td>Trigonal</td>
<td>6.9</td>
</tr>
<tr>
<td>Cr$_7$C$_6$</td>
<td>D5$_{10}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1: Data for chromium carbides

In addition to Chromium, Molybdenum is another element that is present in many structural steels that forms precipitates. Molybdenum forms three carbide phases in Fe-C-Mo alloys. However, alloys of typical Mo content only have one carbide phase present. This phase is (FeMo)$_6$C$_6$, although the proportions present are more typically Fe$_5$Mo$_9$C$_2$. The other two phases of carbide that can be formed are (FeMo)$_7$C$_{15}$ and MoC. Molybdenum will be shown subsequently to form both borides and phosphides in certain steels as well.
7.2 Review of the available literature

Considerable work can be found in the literature regarding precipitation in a number of metal alloys. However, of direct interest to the work of this Thesis is the precipitation of $M_{23}C_6$ in austenitic stainless steels. A number of papers discussing this phenomena will be discussed in the following section. In addition, the precipitation behaviour of ferritic pressure vessel steels will also be generally introduced.

7.2.1 $M_{23}C_6$ precipitation in austenitic steels

Carolan and Faulkner\textsuperscript{[143]} observed the precipitation of $M_{23}C_6$ in Alloy 800\textsuperscript{1}. The samples were aged for times ranging from 1 to 320 minutes and the ageing temperatures ranged from 916 to 1124K. In all, a time/temperature matrix gave 30 combinations. The precipitate behaviour could therefore be related to temperature or time effects, and the results could be compared to the theoretical model described later. In addition to examining precipitate growth in terms of time and temperature, the work also examined the morphology of the growing precipitates. Again, the results obtained from this analysis were also compared to theoretical predictions obtained from the model used.

The results indicated that the most commonly occurring morphology was the cap shape, followed by conical and faceted. There were no disc shaped precipitates observed in any of the samples. The observed precipitate behaviour also appeared to be in close agreement to the theoretically determined values. This will be discussed more when the model is introduced.

Karlsson and Norden\textsuperscript{[74]} examined the precipitate behaviour in AISI 316L and Mo-free AISI 316L stainless steels. This paper is one of a series of papers that examined the influence of boron additions to the microstructure of the steel due to non-equilibrium segregation. In contrast to the work of Carolan and Faulkner, the samples examined in these papers were subjected to heat treatments followed by a range of quenching procedures. These quench procedures varied in start temperature and cooling rate. The start temperatures were 800, 1075 or 1250°C, with quench rates ranging from 0.29 through to greater than 600°C/s.

The observations showed the formation of $M_3B$, $M_3B_2$ and $M_3B_3$ precipitates in the high B 316L steel cooled from 1250°C at 13°C/s. These precipitates have tetragonal

\textsuperscript{1} Alloy 800 has a composition of Fe-33%Ni-20%Cr, with additions of C, Si, Mn, Al and Ti. The alloy was developed in the late 1940's as an low-nickel content alternative to super-alloys, since nickel supplies at the time were scarce. The alloy had good corrosion and oxidation resistance together with good mechanical properties. The material was also easily fabricated. The alloy has found use in the cooling circuitry of many nuclear reactor systems, competing with 316 and 304 stainless steels which are also commonly used.
structures, and had a 'plate-like' morphology. In the material that had been cooled more slowly or cooled from a lower starting temperature, only $M_2B_2$ precipitated. In the Mo-free steel, the precipitation behaviour was somewhat different. The precipitates nucleated and grew more rapidly, and were orthorhombic $M_2B$. This paper made the conclusion that non-equilibrium boron segregation can alter the precipitate behaviour, and the boron and molybdenum appeared to have some form of synergistic effect on the grain boundary composition and precipitate characteristics.

Liu and co-workers[142] examined the precipitate behaviour of irradiated type 304 and 304L stainless steels. These materials are typically structural materials in LWR systems, since they offer good corrosion resistance and good ductility and toughness characteristics. This grade of material is also used as radiation shields within the RPV of PWR systems. The materials do, however, suffer from irradiation assisted stress corrosion cracking (IASCC) owing to preferential chemical attack at the grain boundaries of the alloy. This process is usually attributed to segregation of alloying elements in the region adjacent to the grain boundary. This work, however, examines how segregation and phase transformation influences the IASCC characteristics.

The work irradiated a range of samples at 420 and 550°C with 5MeV H$^+$ to doses of 0.01, 0.1 and 1 dpa. These irradiation conditions are somewhat different to those typically found in LWR systems. The energies of the protons are significantly higher than the neutron energies obtained from uranium fuelled reactors. The observations showed that irradiation of the 304 samples promoted the precipitation of chromium-rich $M_{23}C_6$, and that increasing irradiation fluence caused the growth of these precipitates. This precipitate behaviour was attributed to both the effects of carbon concentration within the material and the irradiation enhanced diffusion of chromium. The carbon concentration of this material is 0.077wt%, which was calculated to be a super-saturation. This, combined with the enhanced diffusion of chromium due to irradiation, promoted the formation of chromium-rich carbides along the grain boundaries of the alloy.

The behaviour of the low-carbon material (304L) was markedly different. Irradiation of the samples caused a phase change from austenite to ferrite to occur. Along these austenite/ferrite boundaries, it was found that $M_{23}C_6$ precipitated. In addition, in these ferrite regions, it was observed that higher neutron fluences caused an increase in both precipitate size and number density. The phase change in the low carbon material was attributed to the $M_{23}C_6$ carbides reducing the carbon concentration within the bulk of the material. This would decrease the stability of the austenite, which could then transform to ferrite, with a bcc structure.

### 7.2.2 Precipitation in RPV steels

Suzuki and co-workers[143] discussed the effect of phosphorus and molybdenum interactions on the thermally induced precipitation of Fe$_3$Mo in Fe-Mo-P alloys. The reason for
this investigation was the assumption that any positive interaction between the two elements would enhance the rate of precipitation. The elements in question both readily segregate, and have been shown by other workers to have some form of interactive behaviour. A range of alloys were considered, each with different molybdenum and phosphorus contents. The workers used the technique of Mössbauer spectroscopy to determine any elemental interaction. The results indicated that the addition of phosphorus to a Fe-3Mo alloy caused the rate of precipitation and growth of Fe$_2$Mo precipitates to increase. The precipitates themselves contained around 9%P, with the concentrations of Fe and Mo being 65% and 26% respectively. These results are significant, since they highlight the effect that minor solute additions may have on precipitation behaviour, owing to different diffusion characteristics.

Using the technique of Atom Probe Field Ion Microscopy (APFIM), Miller and Burke\cite{38} have investigated the precipitation behaviour of neutron irradiated A533B submerged arc weld metal. The paper also discussed some aspects of radiation induced segregation, which have been discussed in detail in Chapter 6. It was found that M$_3$C and molybdenum carbides (Mo$_2$C) were present in the alloy. The composition of these precipitates was approximately 63.6%Mo, 31.4%C, 2.4%Fe, 2.1%Mn, 0.26%O, 0.17%Ni and 0.09%P. Their results also showed that at the carbide-ferrite interface, some phosphorus enrichment was found.

Additionally, grain boundary copper-manganese precipitates with a f.c.c. cubic structure were found in the same neutron irradiated material. These precipitates were typically 300-600nm in length, with a composition of approximately 84%Cu, 14%Mn, 1.5%Ni and 0.5%Fe. However, at the matrix-precipitate interface of these precipitates, enrichments of manganese and nickel were found. A composition profile across such an interface is shown in Figure 7.4. It can be seen that the manganese enrichment was 2.5 times the value within the precipitate, and that the nickel was almost 4 times the concentration found within the particle.

In a vanadium containing steel from the Gundremmingen KRB-A reactor, intragranular vanadium carbo-nitride precipitates of roughly 10nm diameter were found. Analyses of these precipitates showed that phosphorus was present both within the precipitate, as well as adjacent to the precipitate in the ferrite matrix. These precipitates were seen to contain virtually no molybdenum, manganese or chromium.
In the same work\cite{38}, irradiated high molybdenum and phosphorus A533B steel was analysed for precipitate content. The results indicated that following the neutron irradiation to a relatively low fluence of $8 \times 10^{21} \text{m}^{-2} (E>1\text{MeV})$ molybdenum phosphides formed. However, in a model alloy of Fe-0.67\%Ni-0.22\%Cu-0.041\%P, following irradiation to a fluence of $4.6 \times 10^{23} \text{m}^{-2}$, $E>1\text{MeV}$, copper phosphides were observed.

During irradiation of A533B type RPV steels, the formation of ultra-fine copper clusters is observed. At low fluence irradiations (less than $10^{22} \text{m}^{-2}$, $E>1\text{MeV}$), diffuse copper atmospheres form. These atmospheres are regions of solute enrichment, and as such cannot be classified as precipitates. Owing to the high resolution of the atom probe, the observation of these atmospheres is straightforward, since individual atoms can be identified. This permits the formation of a ‘map’ of the atoms present in a small volume of material, which in turn highlights the presence of these atmospheres.

At higher neutron fluences ($10^{23} \text{m}^{-2}$, $E>1\text{MeV}$), copper precipitates become visible. Typically, these precipitates are only a few nanometres in size. Again, APFIM is the ideal technique to observe particles of this size. The composition of these precipitates is approximately 37\% copper, with significant enrichments of nickel, manganese and silicon compared to the bulk material. In many cases, phosphorus segregation has been observed adjacent to these particles.

Miller and co-workers\cite{107} have also characterised the precipitates within neutron irradiated Russian VVER-type RPV steels. As with the previous work, the segregation behaviour of this material has already been discussed in some detail. These materials differ in composition from A533B RPV steels in a number of ways. In particular, the phosphorus and sulphur concentrations found in A533B steels are lower than those found in the Russian VVER RPV steels.
The materials exhibited similar ultra-fine films of molybdenum carbo-nitrides along grain boundaries. These molybdenum carbo-nitride precipitates were less than 1nm in diameter. Phosphorus was also found to segregate to these boundaries. Precipitates containing both copper and phosphorus were also observed. Typically, these precipitates were 0.5nm in diameter and 1.5nm in length.

Miller and Russell[36] performed further analyses on these Russian grades of steel. The copper clusters, which were found in the irradiated but not the un-irradiated control material, were found to also contain manganese, silicon and phosphorus. A high number of phosphorus clusters were also observed in the irradiated material. These clusters were very small, typically containing between 4 and 10 atoms. However, their density was far higher than the copper clusters that had been observed. A figure of $1 \times 10^{24}$ m$^{-3}$ was quoted.

Intragranular vanadium carbo-nitrides were observed both in the irradiated material as well as the un-irradiated samples. These spherical precipitates were between 5 and 10nm in diameter. Phosphorus was also observed to be associated with these precipitates, being detected both within the precipitates as well as at the precipitate/matrix interface. Similar precipitates were also observed along lath and grain boundaries, although these precipitates appeared more irregular in shape, with some precipitates appearing to be lenticular. Again, the size range of these precipitates was between 5 and 10nm.

The technique of APFIM to characterise precipitates within irradiated material has also been used by Pareige and co-workers[144]. The material being studied was a Fe-Cu-Ni model RPV steel alloy, and comparisons were observed between irradiated and un-irradiated samples. The irradiated material, whose composition was Fe-0.25Cu-0.74Ni, was neutron irradiated at 288°C for 1600 hours at a neutron fluence of $4.6 \times 10^{19}$ n/cm$^2$ (E>1MeV).

The thermally aged material, having a composition of Fe-1.28Cu-1.43Ni, was aged at two temperatures, for a range of times. The temperatures selected were 400 and 500°C, with ageing times ranging from 1 to 100 hours. Following the ageing and irradiation processes, the samples were analysed using the ORNL energy-compensated APFIM.

In both aged and irradiated material, copper precipitates were found. However, the composition of these precipitates differed. In the thermally-aged material, the precipitates analysed exhibited nickel enrichments of between 1.5 and 2.5 times, depending upon the length of time the material had been aged. The irradiated material exhibited copper precipitates consisting of far higher enrichments of nickel, typically in the order of 10 times. The size of these precipitates was remarkably small. In the irradiated samples, the sizes of the copper precipitates and clusters analysed were typically of the order of a few nanometres. The thermally aged material exhibited a larger size range of precipitates, ranging from ~5nm in the 400°C and 500°C, 1 hour aged material, to ~20nm in the 500°C, 100 hours aged samples.

Auger and co-workers[145] analysed copper 'clustering' in two model Fe-Cu alloys and a French RPV steel. The process of clustering is subtly different to that of precipitation. A
cluster is a more loosely packed region of an alloy, having the same lattice structure and no distinct interface. Precipitates, as has been shown, have distinct morphologies, lattice structures and interfaces. The clusters investigated were of the region of a few nanometres in size. This size of feature is particularly difficult to observe using conventional TEM techniques, and therefore required a different approach.

In this work, the techniques of APFIM and tomographic atom probe (TAP) were used. The Chapter discussing analytical techniques has introduced the APFIM and has shown that it is of use where structure on an atomic scale is needed. The technique of TAP is a further development of the atom probe, which can image samples on an atomic level. The technique can produce three-dimensional output of the locations of the various atoms present in the material. Thus, it is possible to examine these clusters and other fine features on a sub-nanometre scale.

The results obtained from the RPV steel samples showed that the size and microstructure of the copper clusters were relatively independent of the neutron fluence irradiating the material. However, the number of clusters formed increases with increasing neutron fluence. It was proposed that this increase in cluster density within the material be related in some way to irradiation induced defects and displacement cascades that occur.

Morgan and co-workers[113] observed the behaviour of FV448 martensitic steel during irradiation. Details of the material composition and irradiation conditions have been presented previously in Chapter 6. Prior to irradiation, the alloy exhibited irregularly shaped precipitates of $M_{23}$, located both intra-granularly, and at prior austenite grain boundaries, together with intragranular spherical NbC particles. Following irradiation at 400 and 465°C, the prior austenite grain boundaries became heavily decorated with particles of both $M_{23}$ and $M_6$. Observations of χ-phase particles were also observed intra-granularly.

Precipitation behaviour in ferritic steels during irradiation has been analysed by Mahon and co-workers[39]. The alloy was an Fe-12%Cr ferritic steel, with additions (less than 1%) of nickel and manganese, and traces of molybdenum, silicon, vanadium, phosphorus, carbon, oxygen and nitrogen. In total, six heats of the alloy were analysed after irradiation in either a HVEM or the Variable Energy Cyclotron (VEC). The HVEM irradiation conditions were 10dpa at a rate of $2.7 \times 10^3$ dpa/s, with temperatures ranging from 350 to 650°C. In contrast, the VEC irradiation conditions were 10dpa at the slower rate of $2.7 \times 10^4$ dpa/s, at the temperature of 550°C.

The results indicated that irradiation induced the precipitation of $M_{23}$ grain boundary precipitates in those alloys which contained either molybdenum or vanadium. This precipitation behaviour is remarkable, since the alloys exhibited grain boundary depletion of chromium during irradiation. This would therefore suggest that the kinetics of precipitation are more dominant in these alloys than the kinetics of segregation, since the chromium depletion occurring at the boundary could arise from boundary diffusion of the chromium to the growing precipitates.
Finally, Buswell and co-workers\cite{146} have examined the microstructural changes that occur in RPV steels during irradiation. The materials examined were Japanese A533B steels. In all, 10 alloys were analysed, whose compositions are shown in Table 7.2.

The samples were irradiated in a flux converter rig in the heavy water moderated PLUTO materials test reactor at Harwell. The irradiation conditions were 14 mdpa \( (9 \times 10^{22} \text{n/m}^2, E>1\text{MeV}) \) at a rate of \( 5.9 \times 10^{9} \text{dpa/s} \) \( (3.8 \times 10^{16} \text{n/m}^2/s, E>1\text{MeV}) \) at 290°C.

Samples were analysed using small angle neutron scattering (SANS), TEM and FEGSTEM. The results from the microstructural analysis were correlated to changes in yield stress and hardness changes within the samples.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Mo</th>
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<th>Cu</th>
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<td>0.017</td>
<td>1.41</td>
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<td>0.78</td>
<td>0.54</td>
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<td>0.15</td>
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Table 7.2: Compositions of Japanese A533B RPV steels analysed by Buswell and co-workers\cite{146}

It was found that copper-rich precipitates were present in the materials following irradiation. These precipitates were of the order of 2nm in diameter, and contained manganese and nickel. Owing to the small size of the precipitates, it was difficult to observe them using TEM or FEGSTEM. However, data obtained from the SANS analyses could be interpreted to obtain the precipitate size data. The precipitate composition was also found to vary according to the nickel concentration of the material. The volume fraction of precipitate observed in the samples was also found to increase in proportion to the bulk copper content, as well as in proportion to bulk nickel content at constant copper content. The material hardness was found to correlate well to the size of the copper-rich precipitates within the material. Precipitates of less than 1.5nm in diameter had little effect on the hardness. Larger precipitates, up to 2.5nm in diameter, caused a dramatic increase in material hardness.
7.3 Summary of theoretical precipitation modelling

The modelling of precipitation behaviour in alloys has followed many varied paths. What distinguish the various attempts are the mathematical approaches that are used. Workers have used analytically based models, whereby a series of mathematical equations are solved for the various precipitation conditions. These models will be discussed in some detail, since this is the form of the modelling that has been adopted for this work. Other workers have taken the approach of Monte Carlo modelling. This area of modelling relies on statistics and random probability, and some could argue, is more realistic than any other modelling approach, since nature is entirely random. A particularly useful aspect of Monte Carlo simulations is the inclusion of radiation effects into the predictions. This work has been performed by Saito[147] and Liu[148] for thermally-induced precipitation, and by Soisson and co-workers[149] for irradiation-induced precipitation. This modelling approach, however, is not considered in this work.

The grain boundary precipitation models of Aaron and Aaronson[150], Caisley and Faulkner[151] and Faulkner and Carolan[141,152] assumed a lenticular shaped precipitate morphology and a constant collector plate size with regard to the solute supply. Some consideration of a variable collector plate size was made by Carolan and Faulkner, who concluded that this model was applicable only at temperatures close to the precipitate solvus. Mass transfer to assist growth was assumed to take place by a combined lattice and grain boundary diffusion controlled mechanism. Nucleation was also included in the kinetics appraisal and, for the case of \(\text{M}_2\text{C}_3\) in an austenitic steel matrix, the nucleation kinetics were lattice diffusion controlled. Other work on aluminium alloys by Aaronson’s group highlighted the importance of grain boundary diffusion in this process, but this was probably because the precipitate matrix interfaces (\(\theta\)-prime in Al-Cu) were semicoherent in their work.

Previous attempts at modelling grain boundary precipitation growth behaviour have been performed by Aaron and Aaronson[150], Caisley and Faulkner[151] and Faulkner and Carolan[141]. The theoretical approach of these models assumed a constant collector plate approach to the growth. This limited the applicability of these models since no form of coalescence of particles could take place, which in turn would alter the collector plate area. In addition, the models relied on experimental observation of particle spacing to provide the data as to the size of the collector plates used in the calculations.

7.3.1 Aaron and Aaronson’s model

Aaron and Aaronson investigated the growth of precipitates along grain boundaries in an Aluminium alloy containing 4% copper. The rate of growth of the precipitate was found observed orders of magnitude larger than the diffusion of the solute species within the matrix of the alloy. In addition, experimental work suggested that the rate of precipitate thickening (in directions perpendicular to the grain boundary) was different to the lengthening rate of the precipitate along the grain boundary.
7.3.1.1 Precipitate morphology

The precipitate morphology used by Aaron and Aaronson can be found in Figure 7.5. The precipitate is disc shaped in the plane of the grain boundary, of radius $R_1$. The thickness of the precipitate perpendicular to the grain boundary plane is given by $s$, and the radius of curvature of the precipitate is given by $R_2$. Precipitates of this morphology were experimentally observed in the aluminium alloy aged at a range of temperatures over a range of times. Some faceting of the precipitates was observed, but this was only after prolonged ageing times. During shorter ageing times, little or no faceting was observed.

![Figure 7.5: Precipitate morphology of Aaron and Aaronson](image)

7.3.1.2 Collector-plate modelling approach

The growth of the grain boundary precipitate was modelled using a combination of diffusion parameters. Initially, volume diffusion, $D_v$, of the solute species to a 'collector plate' on the grain boundary occurred, followed by grain boundary diffusion, $D_b$, of the solute species towards the interface of the developing precipitate. This collector plate idea can be shown schematically in Figure 7.6. The area of the collector plate is taken to be the square of the inter-particle distance. This area is significantly larger than the area of the precipitate.

![Figure 7.6: Schematic of collector plate model around growing precipitate](image)
7.3.1.3 Modelling details

The length and thickness of the precipitate were modelled separately, since it was felt that the mechanisms were different for each of the growth rates. This was in part due to the assumed shape of the growing precipitate. The mathematics of the two models can be described using the following series of equations.

The mass transport rate of solute to the precipitate can be expressed in terms of either lengthening or thickening of the growing precipitate. Thus, for precipitate lengthening, the mass transport rate of solute is:

\[
\frac{dm}{dt} = \frac{A_v D^2}{\pi} \left( x_{a} - x_{a(t)} \right) \rho_s^{a} t^{-\frac{1}{2}}
\]

(7.3)

where:  
- \( A_v \) is the interparticle spacing  
- \( D \) is the volume diffusion coefficient for the solute in the matrix  
- \( t \) is the time  
- \( \rho_s^{a} \) is the partial molar density of solute in the matrix  
- \( x_{a(t)} \) is the concentration of solute in equilibrium with the precipitate at the temperature concerned, modified for the Gibbs-Thompson effect  
- \( x_{a} \) is the solute concentration of the matrix.

The Gibbs-Thompson effect allows for the effects of interface curvature on solute solubility in very small precipitates. Thus, in the aluminium-copper system modelled by Aaron and Aaronson, the parameter \( x_{a(t)} \) defined the mole fraction of copper present in the matrix material at the curved edges of the precipitate. The Gibbs-Thomson equation can be determined from:

\[
x_{a(t)} = x_{a}^{0} \left( \exp \left( \frac{\sigma_{a9} V_{Cu}^{a}}{R T R_{2}} \right) \right)
\]

(7.4)

where:  
- \( x_{a}^{0} \) is the concentration of solute in the matrix at the precipitate interface  
- \( \sigma_{a9} \) is the interfacial energy of the \( \alpha:\theta \) interface.  
- \( V_{Cu}^{a} \) is the partial molar volume of Cu in \( \alpha \).  
- \( R \) is the gas constant  
- \( T \) is the absolute temperature.

This relationship can also be determined from:

\[
\frac{dm}{dt} = \frac{dV}{dt}
\]

(7.5)

where:  
- \( V \) is the volume of the newly created phase.
\[
\frac{dm}{dV} = (x_\theta - x_{\alpha(t)}) \rho_s^a
\]

\[
\frac{dV}{dt} \text{ is the rate of change of volume of the precipitate, from } \frac{dV}{dt} = 2\pi R_1 \frac{dR_1}{dt}
\]

From Equation (7.5), it is therefore possible to determine the length, \(R_1\), of the growing precipitate as a function of the parameters introduced. The length can thus be expressed as:

\[
R_1 = \left[ \frac{2(x_\theta - x_{\alpha(t)}) A_\gamma D_2^{1/2}}{\pi^{3/2} (x_\theta - x_{\alpha(t)}) R_2} \right]^{1/4}
\]

(7.6)

For the thickening mechanism of precipitate growth, the expression becomes:

\[
\frac{dm}{dt} = \frac{2\pi R_1 D_{\alpha\theta} (x_{\alpha(t)} - x_{\alpha}) \rho_s^a}{\beta R_1}
\]

(7.7)

where: \(\delta\) is the width of the grain boundary

\(D_{\alpha\theta}\) is the solute diffusivity along the precipitate:matrix interface

\(\beta\) is the average fraction of the interface of radius \(R_1\) that a solute atom diffuses along prior to being absorbed by the growing precipitate, and is equal to

\[
\beta = 1 - \frac{\sqrt{2}}{2}
\]

As with the approach described for the lengthening mechanism earlier, this mass transport rate can also be determined using the relationship shown in Equation (7.5). In the case of the thickening mechanism, the rate of change of volume of the precipitate can be determined from:

\[
\frac{dV}{dt} = \pi R_1^2 \frac{ds}{dt}
\]

(7.8)

Therefore, the thickness of the growing precipitate can be expressed as:

\[
s = 2 \left[ \frac{2D_{\alpha\theta} \left( \exp \left( \frac{D_{\alpha\theta} V_{\gamma}}{RT R_2} \right) - 1 \right) x_{\alpha}}{\beta \kappa^2 (x_\theta - x_{\alpha(t)})} \right]^\frac{1}{2}
\]

(7.9)

For the lengthening of the precipitate, the model assumed that the process was primarily volume diffusion to the (\(\alpha:\alpha\)) grain boundaries followed by boundary diffusion to
the developing precipitate. It was found experimentally that this growth could be modelled using a $t^{0.27}$ relationship. The model predicted this value to be $t^{0.25}$.

Thickening of the precipitate was modelled by diffusion of solute along the matrix to precipitate ($\alpha$:$\beta$) interface. Experimentally, the thickening followed a $t^{0.31}$ relationship. The model developed predicted this relationship to be $t^{0.5}$.

7.3.2 Faulkner and Calsley’s model
This work examined the kinetics of precipitate growth in Nimonic PE16. The modelling aspect of the work was based on the Aaron and Aaronson model discussed previously. However, modifications were made which assumed that the aspect ratio (length to thickness) of the precipitate remained constant, making the mathematics of the model much simpler. The morphology of the precipitate being modelled remained the same as that of the original model, shown previously in Figure 7.5.

7.3.2.1 Modelling details
In this simplified model, it was assumed that the rate-controlling process of precipitate lengthening was one of two possible processes. These processes were either the rate of solute arrival to the precipitate from the collector plate, or the diffusion rate of the solute along the matrix:precipitate ($\alpha$:$\beta$) interface.

If the process is considered to be the rate of solute arrival from the collector plate, then assuming that the aspect ratio of the precipitate remained constant, the rate of change of volume of the precipitate can be expressed as:

$$\frac{dV}{dt} = 3\pi k_1^2 s^2 \frac{ds}{dt}$$  \hspace{1cm} (7.10)

where: $k_1$ is the aspect ratio of the precipitate, from $R_i = k_1 s$

Substituting this equation for the rate of change of volume into Equation 7.5 allows the rate of change of precipitate thickness to be determined:

$$\frac{ds}{dt} = \frac{A_0 D^2}{3\pi k_1^2 s^2} \left( x_\alpha - x_0 \right) \left( x_\beta - x_0 \right)$$  \hspace{1cm} (7.11)

Integrating this equation gives the time as a function of precipitate thickness for a constant aspect ratio:

---

2 Nimonic PE16 is a nickel-chromium base high temperature alloy, containing approximately 75% Ni and 20% Cr. The alloys form a tough oxidation-resistant matrix at high temperatures. Additions of titanium, cobalt, zirconium, aluminium and carbon are found to assist the material in resisting creep at high temperatures by forming carbides.
\[
t = \frac{s^6 \pi^2 k_f (x_0 - x_{\alpha}^{eq})^2}{4A_0 D (x_\alpha - x_{\alpha}^{eq})^2} \quad (7.12)
\]

Thus, the precipitate thickness, \(s\), is related to time, \(t\), to the power of 1/6.

Alternatively, if it is assumed that the rate controlling factor is the diffusion of solute along the matrix:precipitate interface, then the rate of change of precipitate thickness can be determined from:

\[
\frac{ds}{dt} = \frac{2\delta D_{\alpha\beta} (x_{\alpha}^{eq} - x_{\alpha}^{eq})}{3\beta k_f^2 s^2 (x_\alpha - x_{\alpha}^{eq})} \quad (7.13)
\]

Integrating this equation gives the time to grow a given size of precipitate:

\[
t = \frac{s^3 k_f^2 \rho (x_\alpha - x_{\alpha}^{eq})}{2\beta D_{\alpha\beta} (x_{\alpha}^{eq} - x_{\alpha}^{eq})} \quad (7.14)
\]

Thus, thickness, \(s\), is related to time, \(t\), to the power of 1/3.

A simplified equation to determine the equilibrium solute concentration at the precipitate:matrix interface was also developed. This can be expressed as:

\[
(x_{\alpha}^{eq})^{xe} (C_C) = \exp \left( -\frac{\Delta H}{RT} + C \right) \quad (7.15)
\]

where: \(xe\) is the ratio of \(M\) to \(C\) in a \(M_{\alpha\beta}C\) carbide.

\(C_c\) is the carbon concentration.

\(\Delta H\) is an enthalpy connected term.

\(C\) is a constant, from \(C = \frac{\Delta S}{R}\)

\(\Delta S\) is an entropy connected term.

\(R\) is the gas constant.

\(T\) is the absolute temperature.

The solubility product, \(x_{\alpha}^{eq}\), can be plotted as a function of the carbon concentration, as shown in Figure 7.10. It can be seen that increasing ageing temperatures cause the value of \(x_{\alpha}^{eq}\) to increase for a constant carbon concentration. Conversely, maintaining a fixed value for \(x_{\alpha}^{eq}\) requires an increasing carbon concentration as the ageing temperature of the material increases.

From experimental observations of \(M_{234}\) in the PE16 alloy, it was shown that the model governed by solute diffusion across the collector plate gave the best fitting results, rather than the model governed by matrix:precipitate diffusion. In addition, the collector plate model requires fewer parameters. The comparison between the predictions and
experimental observations can be seen in Figure 7.8, which plots time against temperature for the growth of 2.5x10nm constant aspect ratio precipitates.

Figure 7.7: Variation of solute and carbon solubility with temperature

Figure 7.8: Comparison of theoretical predictions and experimental observations of $M_{23}C_6$ precipitate behaviour (from Faulkner and Caisley)

7.3.3 Carolan and Faulkner’s model

Carolan and Faulkner took the theories of Faulkner and Caisley and Aaron and Aaronson and after a number of modifications applied them to the growth of $M_{23}C_6$ precipitates in an Alloy 800. The experimental observations of the precipitate behaviour of this alloy system have already been discussed in detail in Section 7.2.1. They modified the theory to take into account the nucleation kinetics theory of Russell. In additional, the influence of particle morphology was included. This was in contrast the approach of Faulkner
and Caisley, who assumed that the precipitate morphology was the same as that used by Aaron and Aaronson with the inclusion of a constant aspect ratio.

Finally, the growth of the precipitate was modelled by allowing for a range of collector plate geometries. Collector plates were modelled that were both constant and variable in size. A variable collector plate approach was considered, since during nucleation processes the size of the collector plates used in the Faulkner and Caisley model was thought to be unrealistically large.

### 7.3.3.1 Precipitate morphologies

The morphologies that were considered in the modelling approach were disc-shaped, caps, faceted and conical geometries. The disc geometry has been illustrated in Figure 7.6. Details of the other morphologies can be seen in Figures 7.9(a) to (c).
The main feature of the model developed was the inclusion of nucleation kinetics. The basic equation determining the time for nucleation, $\tau$, was expressed as:

$$\tau = \frac{2kT a^4 \sigma_{\alpha\beta} K_j}{V_\alpha \Delta G_v^2 D_v X_\beta L_j}$$

(7.16)

where: $a$ is the lattice parameter.
$V_\alpha$ is the atomic volume of the solute atom.
$\Delta G_v$ is the volume free energy change during the precipitate formation.
$D_v$ is the volume diffusion coefficient.
$X_\alpha$ is the mole fraction of solute in the matrix material.
$K_j$ and $L_j$ are shape factors for precipitate nucleation.

The growth times for the precipitate were dependent upon the collector plate geometry being considered. The equations used for these growth times were extensions of the equations of Faulkner and Caisley. For a constant square collector plate area, the time, $t$, necessary to grow a precipitate of length $L$ can be determined from:

$$t = \frac{\pi^{3/2} f(\psi)^2 \left( X_\theta - X_{\alpha(l)} \right)^2}{4 \pi C^2 D_v \left( X_\alpha - X_{\alpha(l)} \right)^2}$$

(7.17)

where: $f(\psi)$ is a morphological factor.
$A_v C$ is the constant square collector plate area.

For a variable collector plate area, this equation becomes:

$$t = \left[ \frac{3L^{3/2} f(\psi)^2 \left( X_\theta - X_{\alpha(l)} \right)^2}{8D_v^{3/2} \left( X_\alpha - X_{\alpha(l)} \right)^2} \right]^{2/3}$$

(7.18)

It can be seen that the time dependent growth of a precipitate using the constant square collector plate model is related to $L^6$. For the variable collector plate models, this relationship is $L^2$. An example of the model predictions can be seen in Figure 7.9. It was found that for low temperature predictions, the variable collector plate models gave the best predictions when compared to the experimental results. However, at higher temperatures, it was found that the theory became inadequate, since the collector plates began to overlap, which is clearly unrealistic. The constant square collector plate model was therefore more accurate at these higher temperatures.
7.3.4 Jiang and Faulkner

The work of Jiang and Faulkner\cite{Jiang, Faulkner, Chapter5} extended the model of Carolan and applied it to the precipitate behaviour of high strength 7000 series aluminium alloys, in particular, the 7150 system. These alloys were of interest since their stress corrosion cracking resistance was directly related to the dispersion of the grain boundary precipitates, together with the region of solute depletion adjacent to the grain boundary formed during precipitate nucleation and growth. This region is more commonly termed the 'precipitate free zone', or PFZ. The model itself was developed to predict the behaviour of MgZn2 precipitates.

The work showed that using the Carolan and Faulkner model generally underpredicted the observed precipitation behaviour. It was assumed that this under-prediction could be attributed to the segregation behaviour of the alloying elements that form the precipitates. The precipitation model of Carolan was therefore modified to include segregation due to both quenching and ageing. The segregation model adopted for this behaviour was the thermal non-equilibrium segregation proposed by Faulkner\cite{Faulkner}, described in Chapter 5. This model could be used to give predictions of segregation during quenching processes, and could allow for any subsequent segregation of solute during the isothermal ageing process that the material was subjected to. In the alloys considered, the ageing times were very short. Experimentally, ageing times ranging from 30 minutes through to 48 hours were used. These followed from solution treatments at temperatures of 480°C for 20 minutes, and water quenches.

The modelling of precipitate growth also moved away the use of analytical equations to describe the kinetics, in favour of an iterative approach. This approach divided
the precipitate growth into a series of small time intervals, changing the driving force and
segregation parameters in accordance with the precise conditions applicable at each step.
The effect of the segregation behaviour modifies the solute supply rate to the growing
precipitate, therefore affecting the rate of growth of the precipitate.

Two further modifications to the Carolan and Faulkner model were the application of
nucleation equations to define the critical nucleus at the ageing temperature. These
equations also determine the nucleation site density, the reciprocal of which is the collector
plate area at the onset of growth. From the previous discussion of the various models
incorporating collector plate approaches, the definition of the starting conditions are critical in
giving realistic predictions. Recalling the modelling work of Carolan and Faulkner, it was
found that fixed collector plate areas were preferential for either high ageing temperatures, or
for long time periods which would cause overlap between adjacent plates.

Secondly, the assumption of precipitate coalescence was introduced. This effect can
be quantified by calculating the change in collector plate area as a function of time, assuming
that there exists a normal statistical distribution of precipitate sizes. Finally, coarsening of
precipitates is assumed.

The model developed by Jiang and Faulkner is the basis for the modelling work
presented later in this Chapter.

7.3.5 Monte Carlo modelling of precipitation

The modelling of precipitation using Monte Carlo models has been performed by
Saito\cite{147} for thermally-induced precipitation, and by Soisson and co-workers\cite{149} for
irradiation-induced precipitation. The Metropolis Monte Carlo model adopted by Saito
predicted both grain growth and grain boundary precipitation that occur in the austenite to
ferrite transformation of a steel.

The work also examined how different amounts of under-cooling and various grain
sizes affect the predictions. The simulations gave a range of predictions. Precipitates
nucleated at triple points initially, although they subsequently appeared to nucleate along
grain boundaries. Grain boundary migration also appeared to be a possible cause of the
nucleation of precipitates. Increasing the degree of under-cooling of the material caused a
corresponding increase in the rate of nucleation. This also occurred after a decrease in the
initial grain size of the material. Increasing the under-cooling also promoted the formation of
intergranular precipitates.

Soisson and co-workers incorporated the effects of irradiation into a Monte Carlo
simulation technique. The simulations were aimed at investigating the precipitation behaviour
of copper clusters in typical RPV steels. The results from the simulations performed indicated
that the precipitate nuclei formed were very small, typically up to 5nm.
7.4 Details of improved model

The model developed by Jiang and Faulkner, briefly described earlier, has been modified and extended to give predictions for $\text{M}_{23}\text{C}_{6}$ precipitates within an austenitic stainless steel for ageing periods running to tens of thousands of hours. This system has been examined, as there is a considerable amount of experimental data that can be used to verify the predictions. Additionally, the precipitate growth modelling parameters that are required for the theoretical predictions are generally well known.

The main feature of the model is that it incorporates the effects of solute segregation to grain boundaries. The segregation is assumed to be due to the quenching process that the material has been subjected to prior to thermal ageing. Thus, the mechanism can be modelled by TNES, using the model described in Chapter 5. The enrichment adjacent to the grain boundary, formed by the mechanism of TNES, can be used to accelerate the growth of precipitates, since the atoms do not have to diffuse as far to form into the precipitate.

7.4.2 Precipitate nucleation

The nucleation of the precipitates is critical to all subsequent growth predictions. Nucleation governs not only the size of the precipitate, but also the interparticle spacing, which in turn governs the area of the initial collector plate. There are thus three stages to determining the nucleation phase. These stages determine the precipitate nucleus size, the density of nuclei per unit area of grain boundary and finally, the area of the collector plate. The equations used in each of these stages will be explained in the following sections.

7.4.2.1 Precipitate nucleus size

The critical nucleus radius of the precipitate is given by the basic equation of Chadwick. The approach assumes that the formation of the precipitate nucleus causes a change in the energy of the system. The negative component of this energy change is equal to the difference between the free energy per unit volume of the nucleus phase and the matrix phase, and has the nomenclature of $\Delta G_v$. The positive contribution to this energy change is the formation of an interface between the precipitate nucleus and the surrounding matrix material. Assuming that the precipitate nucleus is spherical, this energy is equal to the surface area multiplied by the interfacial energy of the precipitate:matrix interface. The overall energy change, $\Delta G$, is therefore equal to the sum of these energy changes, and can be expressed as:

$$\Delta G = -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \sigma_{00}$$

(7.19)

where: $\sigma_{00}$ is the interfacial energy between the particle and the matrix.

$r$ is the size of the nucleus.
The critical radius of the precipitate nucleus, \( r^* \), can be found from this thermodynamic expression by differentiating the energy change, \( \Delta G \), with respect to \( r \), and then setting the derivative equal to zero. This result can be seen graphically in Figure 7.10. The critical radius is the saddle point of the line representing \( \Delta G \), which has been shown to be equal to:

\[
  r^* = \frac{2\sigma_{\alpha\psi}}{\Delta G_v}
\]

(7.20)

\[\Delta G\]

\[4\pi r^2\sigma\]

\[4/3\pi r^3\Delta G_v\]

Figure 7.10: Thermodynamic barrier to nucleation as a function of nucleus size

The value of the interfacial energy, \( \sigma_{\alpha\psi} \), although assumed to be temperature independent by Chadwick, has since been shown by Murr and co-workers\(^{157,158}\) to vary with temperature. The relationship between \( \sigma \) and temperature can be expressed by:

\[
  \sigma_{\alpha\psi} = \gamma_{gb} - T \left( \frac{d\gamma_{gb}}{dT} \right)
\]

(7.21)

where: \( \sigma_{\alpha\psi} \) is the grain boundary interfacial energy at any temperature.

\( \gamma_{gb} \) is the known grain boundary energy at temperature \( T \).

The data shown in Table 7.3 can be used to determine the grain boundary interfacial energies of a range of alloy systems at any temperature. The system of interest to this theoretical appraisal is austenitic stainless steel, so the data for Type 304 stainless steel is most appropriate. However, the data shown does illustrate the effect that minor additions of phosphorus to alloy systems have on the interfacial energy, as well as its temperature dependence. This factor is worth considering later when predictions are obtained from the model for the precipitate behaviour.
It must also be noted that the formation of a cap-shaped precipitate results in the formation of the two precipitate surfaces, and the corresponding loss of an equivalent area of grain boundary. The two precipitate surfaces formed each have different interfacial energies, since one is parallel to the boundary, and the other is curved. The corrected interfacial energy can be determined from:

$$\sigma = \sigma_{\alpha\beta} + \sigma_{\alpha\beta}^c(\psi) - \sigma_{\alpha\alpha}$$

(7.22)

In Equations (7.20), and all subsequent equations, it is assumed that any reference to the precipitate interfacial energy refers to this corrected energy term. The driving force for solid state transformation, $\Delta G_v$, used in Equation (7.20) to determine the precipitate nucleus critical radius, is given by:

$$\Delta G_v = \frac{RT \ln \left( \frac{x_b}{x_{a\beta}} \right)}{2V_\theta}$$

(7.22)

where: $V_\theta$ is the molar volume of the precipitate phase.

$x_b$ is grain boundary solute concentration.

In Equation (7.22), the term $x_b$ is the grain boundary concentration of the solute element. In the model being developed here, it is assumed that the precipitation process is occurring whilst a material is being aged following a quench. During the quench, it is assumed that thermal non-equilibrium segregation processes can occur. The grain boundary concentration of the solute element will therefore depend upon the segregation that has occurred during the quench process owing to TNES. The term $x_b$ is therefore taken to be equal to $C_x$, which is the grain boundary concentration of the solute element following TNES. The model used for determining the TNES is the same as that presented in Chapter 5.

From the nucleation equations presented thus far, it can be seen that the size of the critical nucleus is dependent upon a number of important variables. Table 7.4 illustrates what happens to the critical precipitate nucleus size owing to changing these critical parameters.
### Table 7.4: Cause and effect of a range of parameter changes

<table>
<thead>
<tr>
<th>Parameter change</th>
<th>Effect on critical precipitate nucleus size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing $C_c$</td>
<td>Decreases</td>
</tr>
<tr>
<td>Increasing $T_s$</td>
<td>Decreases</td>
</tr>
<tr>
<td>Increasing $T_a$</td>
<td>Increases</td>
</tr>
<tr>
<td>Increasing $T_{0,\text{fmp}}$</td>
<td>Increases</td>
</tr>
<tr>
<td>Increasing $\sigma_{\alpha\theta}$</td>
<td>Increases</td>
</tr>
<tr>
<td>Increasing $\sigma_{\alpha\theta}^{C}$</td>
<td>Decreases rapidly (very sensitive)</td>
</tr>
<tr>
<td>Increasing $\sigma_{\alpha\theta}^{m}$</td>
<td>Increases</td>
</tr>
</tbody>
</table>

### 7.4.2.2 Nucleation site density

The number of critical precipitate nuclei per unit area of grain boundary is critical to calculating the collector plate area that is to be used in modelling the growth behaviour of the precipitates. Thus, the nucleation site density function, $N_0$, given by Russell\textsuperscript{153,154} is determined from:

$$N_0 = \frac{N}{x_0} \exp \left( \frac{-\Delta G^*}{kT_{\text{age}}} \right)$$  \hspace{1cm} (7.23)

where:  
- $x_0$ is the solute concentration in the precipitate phase, determined from the precipitate system being modelled.  
- $\Delta G^*$ is the Gibb's free energy of critical grain boundary nucleus formation.  
- $N$ is the number of atom sites at the grain boundary, from $N = d_0 \rho_a N_A$  
- $d_0$ is the grain boundary width.  
- $\rho_a$ is the molar density of the matrix.  
- $N_A$ is Avagadro's number.

The Gibb's free energy of critical grain boundary nucleus formation, $\Delta G^*$, necessary to determine the nucleation site density given in Equation (7.23) can be determined from:

$$\Delta G^* = \frac{4\pi \sigma_{\alpha\theta}^3}{3\Delta G_v^2} \left(2 - 3 \cos(\psi) + \cos^3(\psi)\right)$$  \hspace{1cm} (7.24)

where:  
- $\sigma_{\alpha\theta}$ is the matrix/precipitate interfacial energy.  
- $\psi$ is the angle between the grain boundary and the tangent plane to a precipitate at their intersection.

The angle of intersection, $\psi$, is dependant upon the geometry of the precipitate. From the model of Jiang and Faulkner, a cap shaped precipitate morphology would appear to be the most appropriate geometry to use, with a corresponding grain boundary intersection angle of 57°. This assumption is also backed up by the experimental observations presented later.
7.4.2.3 Nucleation collector plate area

In the approach adopted for this model, it has been assumed that the starting conditions for the collector plate area will be related to the density of the precipitates following nucleation. Therefore, the initial collector plate size, \( A_{m0} \), is the inverse of the number of precipitates per unit area of grain boundary given in Equation (7.23).

\[
A_{m0} = \frac{1}{N_0} \tag{7.25}
\]

This assumption can be assumed realistic since the precipitates will nucleate randomly along the grain boundaries. Following nucleation, it is possible for the size of the collector plate to vary according to the behaviour of the precipitates. Thus, the only method by which the collector plate size can increase is through particle coalescence and coarsening. Coalescence can be important, and we have considered it by assuming that there exists a normal distribution of collector plate sizes about the mean that we have calculated from Equation 7.5. This given by Equation (7.26), where \( A_v \) is the variable collector plate size defined by the normal distribution:

\[
n_0 = \frac{N_0}{2\sqrt{\pi}\sigma} \exp\left[ -\frac{(A_v - A_{m0})^2}{2\sigma^2} \right] \tag{7.26}
\]

where: 
- \( \sigma \) is the standard deviation of the collector plate areas, from \( \sigma = \frac{(A_{m0} - A_{min})}{3} \)
- \( A_{min} \) is the minimum collector plate area, from \( A_{min} = 16D_{bsTa}^2 \)
- \( D_{bsTa} \) is the grain boundary diffusion coefficient of the solute atoms at the nucleation (ageing) temperature
- \( \tau \) is the nucleation time, determined in the following section.

7.4.2.4 Nucleation time

The nucleation times are generally very short at typical ageing temperatures of less than 600°C. The nucleation time is calculated from the equation for cap shaped nuclei determined by van der Velde and co-workers\(^{[160]}\). This equation is slightly different to that used in the model of Carolan and Faulkner presented earlier, and can be expressed as:

\[
\tau = \frac{32kT_{age}a^4\sigma_{eff}^2N_A^2}{D_{bsTa}a^2x_1v_S^2\Delta G_V^s \sin \theta} \tag{7.27}
\]

7.4.3 Precipitate growth by coalescence during ageing

An isothermal ageing process will cause the precipitates to enlarge, either by pure growth or by coalescence of adjacent precipitates. The behaviour of the precipitates will also be governed by the localised segregation within the vicinity of the grain boundary. The model developed here incorporates segregation effects into the predictions of the precipitate growth during the ageing process.
The important requirement of this part of the model is to provide information at any stage in the heat treatment about the amount of segregated solute on the grain boundary. The amount of solute in the solute concentrated layer adjacent to the interface therefore needs to be calculated. The diffusion of the solute will govern the distance that can influence the precipitate growth. Thus, the amount of extra solute, $x_{\text{al}}$ at any time during the ageing process, $t'$, can be given by:

$$x_{\text{al}} = \frac{1}{\Delta l} \int_{0}^{\Delta l} C(y, t')dy$$  \hspace{1cm} (7.28)

where: $\Delta l$ is the solute diffusion distance in the matrix within time $t'$, from $\Delta l = \sqrt{2D_{\text{vst}} t'}$

$D_{\text{vst}}$ is the volume diffusion coefficient of the solute at the ageing temperature.

The ageing process is divided into a number of time intervals. Typically, the model was performed using 1000 time intervals, although higher accuracy of predictions could be obtained using shorter time intervals. During each time interval, the size of the precipitate can be determined, together with the corresponding size of the collector plate area. The representative equation for the precipitate radius, $L_i$, at any time interval, $i$, can be shown by Equation 7.29.

$$L_i = \left(\frac{2A_{\text{m},i-1}D_{\text{vst}}^{1/2}(x_{\text{al}} - x_{\text{al},\text{stage}})^{1/2} - (t' - t_{\text{lag}})^{1/2} \rho_{\text{p}} L_{i-1}^{1/2}}{\rho_{\text{g}} \pi^{3/2} f(\psi)(x_{\text{al}} - x_{\text{al},\text{stage}})}\right)^{1/3}$$  \hspace{1cm} (7.29)

where: $x_{\text{al}}$ is the solute concentration in the precipitate.

$f(\psi)$ is a geometrical parameter dependent on the particle shape

$\rho_{\text{p}}$ is the molar density of the precipitate phase,

$L_{i-1}$ is the precipitate size determined for the previous time.

Of these parameters, $x_{\text{al}}$, $f(\psi)$, $\rho_{\text{p}}$, and the diffusion coefficient, $D_{\text{vst}}$, remain constant.

The collector plate area determined from the nucleation process can also enlarge during ageing. This is determined by assessing the reduction in number of precipitates per unit area owing to the effect of coalescence. The probability of coalescence occurring is given by $n_{\text{c}}/N_0$ taken from Equation 7.26, and so at each time step $A_{\text{c}}$ can be recalculated to give $A_{\text{mn}}$ using the following equation.

$$A_{\text{mn}} = \frac{1}{N_0} \prod_{i=1}^{l=n} \left[ 1 - 0.25 \left( \text{erf} \left( \frac{A_{\text{m},i-1} - A_{\text{m},\text{mn}}}{\sqrt{2} \sigma} \right) - \text{erf} \left( \frac{A_{\text{m},i-1} - 4L_{i-1}^{1/2}}{\sqrt{2} \sigma} \right) \right)^2 \right]$$  \hspace{1cm} (7.30)

where: $A_{\text{m},i}$ is the collector plate area calculated at the previous time interval.

$L_i$ is the precipitate size at the time being considered.

The bottom of this equation is summed throughout the ageing process. The size of the precipitate, $L_i$, is related to the size of the collector plate at the previous calculation time,
Immediately following nucleation, the precipitate is therefore related to the size of the collector plate determined from the various nucleation equations.

In principle, the model can be used not only to calculate precipitate size as a function of quenching and ageing treatments, but also to calculate interparticle spacing, through $1/(A)^{1/2}$.

### 7.4.4 Precipitate coarsening during ageing

The growth of precipitates due to solute segregation has been discussed. However, at long ageing times, another mechanism for precipitate growth may become dominant. This final mechanism of precipitate growth is termed 'coarsening'. The growth of the precipitates during this process is assumed to be due to the combination of the individual precipitates into larger particles. During this regime of growth, it is assumed that the total volume of precipitate that is present within the material does not change with time. Since the total volume does not change, the number of precipitates present within the material decreases, with a corresponding increase in the average particle size.

The effect of coarsening of precipitates at very long ageing times needs to be considered, since many materials used in power generating plant will be in service for ten’s of years. There thus exists a critical time that defines the onset of this final stage of a precipitates life. This critical time can be evaluated from:

$$t_{cc} = \frac{d^2}{8D_{VsTa}}$$  \hspace{1cm} (7.31)

where: $D_{VsTa}$ is the solute volume diffusion coefficient at the absolute ageing temperature.

During this precipitate coarsening regime, the equation for the growth of the precipitate will change, since the mechanism of precipitate growth has changed. Therefore, for any time, $t$, greater than the critical coarsening time, $t_{cc}$, the precipitate size $L(t)$ can be determined from:

$$L(t) = \left[ \frac{9d_0 D_{BSTa} \alpha_{20g} V_b (t - t_{cc})}{32ABRT} + L(t_{cc}) \right]^{\frac{1}{4}}$$  \hspace{1cm} (7.32)

where: $d_0$ is the grain boundary width.

$D_{BSTa}$ is the grain boundary solute diffusion coefficient, calculated at the absolute ageing temperature.

$L(t_{cc})$ is the precipitate size at the onset of coarsening.

The constants A and B in Equation (7.32) can be determined from the following equations. The equation to determine A relates the interfacial energy of a (matrix:matrix) boundary and a (matrix:precipitate) boundary.
\[
A = \frac{2}{3} \left( \frac{1 - \sigma_{oo}}{2 \sigma_{oo}} \right) \\
B = \frac{1}{2} \ln \left( \frac{1}{f} \right)
\]

(7.33) \hspace{1cm} (7.34)

where: \( \sigma_{oo} \) is the matrix-matrix interfacial energy

\( \sigma_{oa} \) is the matrix-precipitate interfacial energy

\( f \) is the fraction of grain boundary plane covered by precipitates at the onset of coarsening, from

\[
f = \frac{\pi L(t_{cc})^2}{A_m(t_{cc})}
\]

Note from the equations presented for the coarsening regime that there is no need to perform these calculations using small time intervals. However, for completeness, the calculations have been performed using the same time increments that were used for the calculation of the precipitate size during growth by solute absorption.

7.5 Results

The model developed here has been applied to the alloys whose respective compositions are listed in Table 7.5. The prime differences between the alloys are the carbon contents, which will obviously affect the rates of carbide nucleation and growth within the systems being investigated. The range of carbon present is 0.034\% in alloy AM to 0.083\% in Alloy AK. Chromium contents are very similar between the three alloys, with figures around 17\%. There is some difference in the manganese contents; Alloy AK has the lowest figure of 0.77\% and Alloy AM the highest with 1.87\%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>B</th>
<th>Nb</th>
<th>Ti</th>
<th>V</th>
<th>N</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>.034</td>
<td>.18</td>
<td>1.87</td>
<td>.021</td>
<td>.013</td>
<td>16.62</td>
<td>2.3</td>
<td>10.45</td>
<td>.0043</td>
<td>.01</td>
<td>.006</td>
<td>.02</td>
<td>.033</td>
<td>.035</td>
</tr>
<tr>
<td>QP</td>
<td>.05</td>
<td>.61</td>
<td>1.75</td>
<td>.031</td>
<td>.01</td>
<td>17.2</td>
<td>2.25</td>
<td>12.2</td>
<td>.0002</td>
<td>.035</td>
<td>.005</td>
<td>.025</td>
<td>.04</td>
<td>.295</td>
</tr>
<tr>
<td>AK</td>
<td>.083</td>
<td>.35</td>
<td>.77</td>
<td>.033</td>
<td>.016</td>
<td>16.7</td>
<td>2.52</td>
<td>11.7</td>
<td>.0001</td>
<td>.083</td>
<td>.035</td>
<td>.77</td>
<td>.0285</td>
<td>.09</td>
</tr>
</tbody>
</table>

Table 7.5: Material compositions

7.5.1 Experimental observations

Experimental observation of \( M_{23}C_6 \) precipitate formation in Type 316 stainless steel has been kindly provided by British Energy (formerly Nuclear Electric plc and the Central Electricity Generating Board). The results of various experimental observations were obtained from internal company reports\(^{[161-164]}\). More recently, observations of precipitation have also been obtained by British Energy. The experimental results obtained are shown in Table 7.6. The data presented indicate the service conditions of the material, together with the precipitate measurements obtained from sample analysis.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ageing temp (°C)</th>
<th>Ageing time (hrs)</th>
<th>Ppt length (nm)</th>
<th>Ppt width (nm)</th>
<th>Number measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM37</td>
<td>550</td>
<td>103529</td>
<td>354</td>
<td>173</td>
<td>80</td>
</tr>
<tr>
<td>AM12</td>
<td>600</td>
<td>95736</td>
<td>312</td>
<td>144</td>
<td>50</td>
</tr>
<tr>
<td>AM2</td>
<td>650</td>
<td>18686</td>
<td>313</td>
<td>187</td>
<td>25</td>
</tr>
<tr>
<td>QP22</td>
<td>500</td>
<td>59751</td>
<td>101</td>
<td>80</td>
<td>49</td>
</tr>
<tr>
<td>QP35</td>
<td>550</td>
<td>3884</td>
<td>136</td>
<td>86</td>
<td>132</td>
</tr>
<tr>
<td>AK32</td>
<td>600</td>
<td>78591</td>
<td>276</td>
<td>160</td>
<td>48</td>
</tr>
<tr>
<td>AK14</td>
<td>700</td>
<td>5544</td>
<td>240</td>
<td>146</td>
<td>118</td>
</tr>
</tbody>
</table>

Table 7.6: Results of precipitate measurements

Figure 7.11: Micrograph of alloy AK (3600x magnification)

Figure 7.12: Micrograph of alloy AK (13000x magnification)
Figure 7.13: Micrograph of alloy AM (6000x magnification)

Figure 7.14: Micrograph of alloy AM (17000x magnification)
Figure 7.15: Micrograph of alloy QP (3600x magnification)

Figure 7.16: Micrograph of alloy QP (13000x magnification)
7.5.2 Theoretical predictions

The parameters used in the theoretical calculations are shown in Table 7.7. The variable parameters used in the model are the carbon content, the solute content, and the ageing temperature, time and calculation time interval. The carbon and chromium contents of the three alloys can be found from Table 7.5. The ageing processes modelled are temperature ranging from 773K to 923K, with time up to 100 000 hours.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitate/matrix angle, ( \psi )</td>
<td>°</td>
<td>57</td>
</tr>
<tr>
<td>Lattice parameter, ( a )</td>
<td>m</td>
<td>3.649x10^{-10}</td>
</tr>
<tr>
<td>Pre-exponential constant for solute volume diffusion, ( a_v )</td>
<td>m^2.s^{-1}</td>
<td>6.3x10^{-6}</td>
</tr>
<tr>
<td>Activation energy for volume diffusion, ( Q_v )</td>
<td>J.mol^{-1}</td>
<td>243000</td>
</tr>
<tr>
<td>Pre-exponential constant for solute boundary diffusion, ( a_b )</td>
<td>m^2.s^{-1}</td>
<td>0.003</td>
</tr>
<tr>
<td>Activation energy for boundary diffusion, ( Q_b )</td>
<td>J.mol^{-1}</td>
<td>191000</td>
</tr>
<tr>
<td>Vacancy-solute complex binding energy, ( E_b )</td>
<td>eV</td>
<td>0.0361</td>
</tr>
<tr>
<td>Vacancy formation energy, ( E_v )</td>
<td>eV</td>
<td>1.6</td>
</tr>
<tr>
<td>Activation energy for complex diffusion, ( E_a )</td>
<td>eV</td>
<td>1.96825</td>
</tr>
<tr>
<td>Pre-exponential constant for diffusion of complexes, ( D_{oc} )</td>
<td>m^2.s^{-1}</td>
<td>0.00083</td>
</tr>
<tr>
<td>Molar density of matrix phase, ( \rho_a )</td>
<td>mol.m^{-3}</td>
<td>140920</td>
</tr>
<tr>
<td>Molar density of precipitate phase, ( \rho_p )</td>
<td>mol.m^{-3}</td>
<td>5496</td>
</tr>
<tr>
<td>Molar volume of precipitate phase, ( V_p )</td>
<td>m^3.mol^{-1}</td>
<td>0.000181932</td>
</tr>
<tr>
<td>Atomic fraction of solute in precipitate phase, ( x_p )</td>
<td>mol.fr.</td>
<td>0.78</td>
</tr>
<tr>
<td>Interfacial energy of matrix-precipitate interface, ( \sigma_{a9} )</td>
<td>J.m^{-2}</td>
<td>0.668</td>
</tr>
<tr>
<td>Interfacial energy of curved surface of precipitate, ( \sigma_{c9} )</td>
<td>J.m^{-2}</td>
<td>0.448</td>
</tr>
<tr>
<td>Interfacial energy of grain boundary, ( \sigma_{eb} )</td>
<td>J.m^{-2}</td>
<td>1.25</td>
</tr>
<tr>
<td>Radius of advancing precipitate, ( r' )</td>
<td>m</td>
<td>0.0000001</td>
</tr>
</tbody>
</table>

Table 7.7: Parameters used for model predictions

The binding energy between chromium and vacancies, used in the segregation model that has been incorporated into the precipitation model, can be determined from Figure 7.17. This figure also shows the data for interstitial-impurity atom complexes, although these data are not required for the thermal-non equilibrium segregation model.

Figure 7.17: Complex binding energies for impurity atoms within an austenitic matrix (from Song[901])
The precipitate growth predictions obtained from the model for the various alloys and ageing conditions are shown in Figures 7.18 to 7.20. The results are presented in a different form to the Carolan and Faulkner model, owing to the iterative nature of the model. This format shows the precipitate radius as a function of ageing time. The onset of coarsening can be clearly observed by a sudden increase in the precipitate size during service life. The experimentally observed figures are also plotted on the various graphs.

Figure 7.18: Precipitate growth predictions for alloy AM

Figure 7.19: Precipitate growth predictions for alloy QP
Chapter summary

This Chapter has introduced a precipitation model that has been used to predict the nucleation, growth and coalescence of Cr$_{23}$C$_6$ precipitates in an austenitic stainless steel. The predictions show how the precipitates grow during the service life of the material. In the cases highlighted here, service lives running to 100,000 hours have been modelled. The iterative model permits prediction of precipitate size for any time during the overall service life of the material. This is a significant improvement over the previous models of Aaron and Aaronson, Faulkner and Caisley, and Carolan and Faulkner, whose models would only return overall growth times to reach a given size, or precipitate size for a given time. The model presented here also allows for segregation of chromium, both during cooling from heat treatment, and due to service life thermal conditions. The segregation model used is that of thermal non-equilibrium segregation, which has been presented in Chapter 5. The enrichment of chromium adjacent to the grain boundary is assumed to accelerate the rate of growth of precipitate owing to the shorter diffusion distances required. A discussion of the model, highlighting its relative merits and limitations, will be presented in Chapter 9, alongside discussion of the other modelling approaches developed in this Thesis.
Chapter 8: Atomic modelling of segregation

8.1 Introduction

The modelling work presented thus far in the Thesis has concentrated on the analytically based solute drag theories to predict grain boundary segregation, due to both thermal and irradiation effects. The use of more complex Monte Carlo simulation models have been briefly mentioned in Chapter 7 in relation to the nucleation and growth of grain boundary precipitates both during thermal and irradiation conditions. These complex Monte Carlo simulations have also been used with some success to simulate the effect of displacement cascades arising from neutron irradiation. In particular, the research of Bacon and co-workers[16] and Heinisch and Singh[17] have produced interesting predictions.

In this Chapter, a more simple atomistic model will be presented that has been used to predict segregation of elements within a binary matrix. The work presented here extends modelling performed previously by Chapman and Faulkner[88] and Waite and Faulkner[156]. The approach considers interactions between vacancies and substitutional impurity elements, and predicts the segregation behaviour near a grain boundary. The model can therefore be closely compared with the analytical TNES model owing to the mechanism of segregation. The model is also performed at a constant temperature, and models short time periods at this fixed temperature. Owing to the simplifications of the model, whereby only vacancies and impurity atoms are considered, fewer calculations are required per time increment, and thus the model can predict behaviour for longer times than typical Monte Carlo simulations.

8.2 Chapman’s model

Chapman’s model[88] was developed to predict the atomic movement of boron within a simple cubic lattice of stainless steel. The approach adopted a random walk method, whereby the boron impurity atoms and the vacant sites could move randomly through a two dimensional matrix. The vacancies and impurities can therefore be in one of four possible directions, as shown in Figure 8.1. This approach therefore simulates segregation along close-packed atomic planes.

At each new movement, the binding energy of the new site was calculated using the binding energies of vacancy-vacancy, vacancy-impurity, impurity-impurity and grain boundary binding. If the movement to the random new site is energetically favourable, the movement is performed. In order to model grain boundary segregation, the binding of the impurity or of the vacancy was assumed inversely proportional to the distance of the element from the grain boundary. It was also assumed that the vacant sites were annihilated at the grain boundaries.
An aspect of the work of Chapman and Faulkner has already been covered in some detail. Recalling Section 5.3.2.2, a series of formulae were presented which determined the binding energies between solute elements and vacancies. This approach was subsequently extended to consider the binding between impurities and interstitial atoms, necessary for the prediction of RIS, discussed in Chapter 6. These formulae were originally used in the work of Chapman and Faulkner to predict the binding energies for both vacancies and solute atoms for use in the early version of the atomistic model extended here.

Using the formulae presented in Chapter 5, and taking values for boron in a steel matrix, the data in Table 8.1 can be derived.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Migration energy of vacancy</td>
<td>1.6</td>
</tr>
<tr>
<td>Di-vacancy binding energy</td>
<td>0.14</td>
</tr>
<tr>
<td>Vacancy-impurity complex formation energy</td>
<td>0.5</td>
</tr>
<tr>
<td>Vacancy to GB binding energy</td>
<td>1.6</td>
</tr>
<tr>
<td>Migration energy of impurity</td>
<td>1.4</td>
</tr>
<tr>
<td>Di-impurity binding energy</td>
<td>0.12</td>
</tr>
<tr>
<td>Impurity to GB binding energy</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table 8.1: Data for boron in steel from Chapman

8.3 Waite's model

Waite took Chapman and Faulkner's original model and extended it to include a flux of vacancies that were attracted towards the grain boundary to replace those vacancies that had been annihilated at the grain boundary. The method adopted was to assume a diffusion pattern similar to that of the carburisation of a semi-infinite steel block. By using Fick's first law, a vacancy flux towards the grain boundary can be calculated from:
where: $C_b$ is the concentration of vacancies at the grain boundary  
$C_0$ is the current concentration  
$D$ is the diffusion coefficient of vacancies  
$x$ is the distance from the grain boundary  
$t$ is the time.

Substituting the matrix dimensions into the equation allows the determination of the probability of a vacancy entering the matrix in a given time, $dt$, thus,

$$P' = 2(Ddt)^{1/2} s^{-1/2} \exp \left( - \frac{m^2 a^2}{16 D dt s} \right)$$  

where:  
$m$ is the matrix size  
$a$ is the lattice parameter of the matrix  
s is the number of the cycle of calculation.

In addition to introducing a flux of new vacancies to the matrix, Waite also introduced the idea that the defect-defect binding energy varied in relation to the distance from the grain boundary. The basis for this assumption was that in Chapman’s work, there appeared to be little or no desegregation. This was assumed to be because once impurity atoms reached the boundary, they effectively produced a large cluster, which was energetically difficult to be removed from. It was also assumed that since the formation energies calculated for the materials are calculated for a homogenous matrix, the same energies cannot be representative of the region around the grain boundary. Thus, Waite proposed the following equation for modifying the defect-defect energy, which, essentially, is an inverse square law.

$$E = E_0 \left( 1 - \frac{0.25}{S_a S_b} \right)$$  

where:  
$E_0$ is the original binding energy  
$S_a$ is the distance of impurity a to the grain boundary  
$S_b$ is the distance of impurity b from the grain boundary.

The results presented by Waite demonstrated that for boron segregating within a steel matrix, the maximum segregation occurred between 1.2 and 1.5 msec at a heat treatment temperature of 1300K.
8.4 Modifications of the present work

In the current work, the original model of Waite and Faulkner was initially modified so that the program could be run on a standard PC. The results obtained from this new program are shown in Figures 8.2 and 8.3. They present the before and after conditions of the simulation, performed using the data for Boron shown in Table 8.1. The program was run for 20,000 cycles. This represents a real time of 2msec, since each cycle of the program represents 1x10⁻⁷ seconds.

![Figure 8.2](image1.png)

**Figure 8.2:** Randomly generated starting positions of vacancies and boron atoms

![Figure 8.3](image2.png)

**Figure 8.3:** Predicted segregation of vacancies and boron atoms after 20,000 program cycles
One important feature of this type of model is the demonstration of how electron microscopes would observe the data. The graphs in Figure 8.4 and 8.5 show how the use of different 'probe' sizes would adjust the actual results obtained. The figure shows the results obtained using effective probe sizes of 1, 2, 5 and 10 atomic planes. Assuming an atomic plane in a cubic lattice is equivalent to $3.59 \times 10^{-10}$ m, these represent probe sizes of 0.359 nm, 0.718 nm, 1.795 nm and 3.59 nm. Since an average FEGSTEM has a spatial resolution of 3 nm, then the nearest approximation from the results would be that of the average over 10 atomic layers. Examining the graph shows how this figure is far removed from the actual segregation observed when examining each atomic layer in turn.

Figure 8.4: Segregation profile across GB for Boron after 20 000 cycles

Figure 8.5: Predicted segregation profile across GB for Boron after 20 000 cycles
Following the predictions for boron, the segregation of phosphorus was modelled. Data for both chromium and molybdenum were also determined. The data for these elements can be seen in Table 8.2. These figures highlight the low affinity that exists between grain boundaries and chromium.

<table>
<thead>
<tr>
<th>Energy term</th>
<th>Chromium</th>
<th>Phosphorus</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impurity-GB binding (eV)</td>
<td>0.65x10^{-3}</td>
<td>0.17</td>
<td>0.0445</td>
</tr>
<tr>
<td>Vacancy-impurity binding (eV)</td>
<td>0.0361</td>
<td>0.41</td>
<td>0.298</td>
</tr>
<tr>
<td>Impurity-impurity binding (eV)</td>
<td>0.0119</td>
<td>0.043</td>
<td>0.0111</td>
</tr>
<tr>
<td>Impurity migration (eV)</td>
<td>0.86</td>
<td>1.15</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Table 8.2: Data used in current simulation

![Figure 8.6: Randomly generated starting positions](image1)

![Figure 8.7: Predicted segregation of Phosphorus after 100 000 cycles](image2)
Figures 8.6 and 8.7 show the starting conditions and the predictions after 100 000 cycles of the model, which represents 10msec of real time. The results indicate that little segregation has occurred. The results shown do indicate some segregation, but without the definition shown by the results obtained for Boron, presented earlier.

This would indicate that the model needs to be run for a larger number of cycles, since the binding energy of the Phosphorus atoms to the grain boundary is much lower than that of the boron atoms. The figures are 0.17eV for Phosphorus compared to 0.45eV for Boron, calculated using the theory presented by Chapman. The migration energy of Phosphorus is also lower than that of Boron, but not by such a large amount.

Additionally, the predictions for Phosphorus segregation were run using a lower concentration of vacancies than the predictions obtained for Boron. Since the degree of segregation using this model has been shown to be influenced by the vacancy concentration, it will be necessary to obtain predictions for Phosphorus using a vacancy concentration of 0.75at.% instead of the 0.5at.% used in the results presented.

8.4.1 Extension of the model to a 3-D lattice

The two dimensional model used to obtain the predictions shown in the previous section is somewhat limited to the type of segregation that it can model. Considering the case of thermal non-equilibrium segregation presented in Chapter 5, it was shown that the mechanism is that of long range migration of vacancy-impurity atom complexes. These complexes were shown to migrate in three dimensions, were the vacancy and solute atom remain in nearest neighbour configurations. Therefore, in order to model this phenomenon using atomistic simulation, the model must be extended to consider elemental segregation in three dimensions.

8.4.1.1 Simple cubic lattice

The first stage of extending the simulation model is to simply consider a cubic array of atoms, containing a number of vacancies and interstitials. Thus, each site within this array has six nearest neighbours, and thus six directions for migration. To keep the atomic concentration of both impurities and vacancies comparable to those used in the two dimensional simulation, either a smaller matrix size must be used, or a larger number of vacancies and impurity atoms must be considered. For example, a bulk concentration of 0.1 atomic percent requires 40 atoms to be considered in a two dimensional 200x200 matrix. In a three dimensional matrix of 200x200x200, 8000 atoms would be need to be modelled. Alternatively, a matrix of 100x100x100 could be used, with only 1000 atoms required. In either case, there is a significant jump in the number of elements that are considered, and thus the number of calculations, and hence the time required to perform the calculations, increases dramatically.
Figures 8.8 and 8.9 show typical results obtained from this three dimensional model, using a smaller matrix size and an increased number of elements. The same predictions are shown, except in Figure 8.9, the grain boundary, shown by the central line, is aligned with the viewpoint. It can be seen that considerable segregation has occurred during the simulation. The simulation shown uses the data for boron, which was shown to segregate more rapidly than phosphorus, chromium and molybdenum in simulations based on the two dimensional model.

Figure 8.8: Segregation predicted by three-dimensional simple cubic model

Figure 8.9: Grain boundary of simple cubic lattice
8.4.1.2 Further modifications to the model

With the ultimate aim of more precisely modelling the migration of vacancy-impurity atom complexes, the cubic matrix described previously was further modified to consider both body centred cubic and face centred cubic lattice structures. These modifications were relatively straightforward, having determined the geometry and defined the range of movements that each atom could undergo. However, the calculation time required to perform these simulations was longer again than the simple cubic lattice described in the previous section. This was, again, due to the requirement to perform more calculations to simulate the same atomic concentration for the same time. No predictions are presented here, since those that were obtained bore close resemblance to those shown in Figure 8.9.

No further modifications were then made to the model, either to consider the formation and subsequent long-range migration of clearly defined complexes, or to introduce interstitial atoms into the calculations. It was felt that the time constraint was too significant, and thus prevented any real development and application of the simulation.

8.5 Chapter summary

An extended atomistic simulation model has been presented. The model considered both impurity atom and vacancy migration through both two and three-dimensional lattices. In the latter case, both cubic, body centred cubic and face centred cubic lattices have been considered. The elements modelled have been boron, chromium, phosphorus and molybdenum. Of the elements considered, the simulations indicated that boron was the fastest segregating element. The main constraint of the application of the model was found to be the number of calculations, and hence the time, required to simulate typically milliseconds of real time. The aim of the work was ultimately to consider the migration of clearly defined complexes, as well as interstitial atoms. However, this aim was not fully reached owing to this shortfall in the model.
Chapter 9: Discussion

The work presented in this Thesis has covered the observation and theoretical prediction of a range of microstructural phenomena. Experimental observations of grain boundary segregation have been presented in Chapter 4, using a number of techniques that had been previously discussed in Chapter 3. The results presented were for post-weld heat-treated material, analysed using both FEGSTEM/EDXS and AES, together with irradiated material analysed by FEGSTEM/EDXS. The first section of this Chapter will discuss these results, and highlight the relative merits and associated limitations of each of the micro-analytical techniques used.

The theoretical models that have been developed in this work have been presented in Chapters 5 through to 8. The segregation models presented in Chapters 5 and 6 have returned predictions of the grain boundary segregation of a range of the alloying elements in the RPV steels, due to both post-weld heat treatments and to reactor service conditions. In Chapter 7, a precipitation model was developed, and predictions were obtained for chromium carbide growth during long-term service of an austenitic stainless steel. The final model developed in the Thesis was an atomistic simulation of grain boundary segregation due purely to thermal conditions. Discussion of these various models in comparison to the relevant experimental observations will be presented in later sections of this Chapter, together with discussion of the advantages and limitations of the various approaches.

9.1 Discussion of experimental work

In the work presented in this Thesis, a number of experimental techniques have been used to examine and classify the RPV steel. These have included the micro-analytical techniques of FEGSTEM/EDXS and AES. For the post-weld heat-treated material, the aim of the analysis was to accurately measure the grain boundary concentrations of phosphorus, carbon, manganese and molybdenum. The irradiated material was only analysed for segregated phosphorus at the grain boundaries. The results obtained from these analyses, together with the experimental limitations, will be discussed here.

9.1.1 FEGSTEM/EDXS analysis of grain boundaries

The micro-analytical tool of FEGSTEM with EDXS has become the tool of choice for a large number of research groups investigating a range of interfacial phenomena. Owing to its potentially high spatial resolution and non-destructive analysis procedure, its use has become widespread in the area of elemental segregation to grain boundaries. Additionally, owing to the small size and volume of samples required for FEGSTEM analysis, compared to techniques such as AES, the technique has been used widely for examining radiation damage.
The bulk of the FEGSTEM work examining the un-irradiated material was performed on a VG601 FEGSTEM at Liverpool University, using a 10° tilt specimen holder. A number of EDXS analyses were performed, including point analyses along grain boundaries as well as digital linescans across suitably aligned boundaries. In addition, the compositions of a number of grain boundary precipitates were analysed in alloy SG.

The figures obtained for the grain boundary concentrations of phosphorus, molybdenum and manganese are summarised below in Table 9.1. These results express the mean and standard deviation of the observed grain boundary concentrations, measured in wt.% The bulk concentrations of these three elements can be found in Table 4.1. To summarise here, the phosphorus concentration in these alloys is approximately 0.024wt.%, with the exception of alloy SL, which is slightly lower at 0.017wt.%. The molybdenum contents are on average 0.5wt.%, and the manganese contents approximately 1.5wt.%. 

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phosphorus</th>
<th>Molybdenum</th>
<th>Manganese</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF</td>
<td>0.13 (0.08)</td>
<td>1.29 (0.54)</td>
<td>1.00 (0.35)</td>
</tr>
<tr>
<td>SG</td>
<td>0.08 (0.06)</td>
<td>0.54 (0.23)</td>
<td>1.16 (0.41)</td>
</tr>
<tr>
<td>SL</td>
<td>0.08 (-)</td>
<td>0.85 (-)</td>
<td>0.85 (-)</td>
</tr>
<tr>
<td>SP</td>
<td>0.16 (0.10)</td>
<td>0.95 (0.44)</td>
<td>0.99 (0.33)</td>
</tr>
</tbody>
</table>

Table 9.1: Mean and (standard deviation)\(^1\) of Liverpool FEGSTEM results

It can be seen from this data that both phosphorus and molybdenum would appear to be slightly enriched at the grain boundaries compared to the bulk contents of the elements. There is, however, significant spread in the results, as shown by the figures quoted in brackets for the standard deviations. In comparison, the behaviour of manganese is markedly different. The bulk content of manganese in the alloys has been quoted as 1.5wt.%. However, the figures presented here indicate the grain boundary concentrations are typically around 1wt.%. This fact, in isolation, would imply that the manganese has become depleted at the grain boundaries.

However, examination of the linescans shown in Figures 4.14 through to 4.16 would indicate that there is marked grain boundary enrichment of manganese, together with enriched regions extending a few nanometres into the adjacent matrix material. These qualitative observations can be quantified by the point analyses performed across grain boundaries in alloys SP and SF, shown in Figures 4.10 and 4.11. From these analyses, it can be seen that although the grain boundary concentrations are lower than the quoted bulk figures, the matrix material adjacent to the grain boundary has less manganese still. This 'loss' of manganese from the matrix material can be attributed to the precipitation behaviour of the material.

\(^1\) Note: Standard deviations only calculated where 3 or more results were obtained
The data presented in Table 4.6 indicate that in the grain boundary carbides that were analysed, there were significant levels of both manganese and molybdenum. Taking these combined facts into consideration, it can be assumed that the grain boundary precipitation of carbides has removed both manganese and molybdenum from the matrix material. Therefore, the grain boundary enrichments of molybdenum and manganese should be determined from ratio of the observed grain boundary and bulk concentrations, and not the ratio of the observed grain boundary concentration and the bulk contents.

The data shown below in Table 9.2 is a summary of the grain boundary concentrations of phosphorus in three of the post-weld heat treated alloys, obtained from FEGSTEM/EDXS analyses performed at Harwell. Comparison of these results with the results obtained from the work at Liverpool highlights significant differences. The results from Harwell would indicate that the phosphorus is highly enriched at the grain boundaries. In comparison to the bulk phosphorus contents, it can be seen that in alloy SP, phosphorus becomes enriched by over 100 times, with the maximum equating to an enrichment of over 200 times. For alloy SG, the average enrichment is around 65 times bulk content, with a maximum of 115 times.

Perhaps the most significant observation of these results is that some grain boundaries in alloy SP exhibited no phosphorus. Since the exact results are unavailable, it is difficult to comment on how important this is. However, the fact that a zero result was obtained highlights the importance of characterising the type of boundary that is being analysed, for purposes of accurately comparing with alternative data. Likewise, without information regarding the exact experimental techniques employed, further comment on these results is difficult.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GB P (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP72</td>
<td>0</td>
</tr>
<tr>
<td>SG33</td>
<td>0.5</td>
</tr>
<tr>
<td>SL</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 9.2: Harwell results of phosphorus segregation in un-irradiated samples

9.1.2 Limitations of FEGSTEM/EDXS analysis

Examination of the results obtained from the analyses performed at Harwell, and more importantly at Liverpool, highlight a number of limitations of the FEGSTEM/EDXS technique. The spread that appears in the Liverpool results presented can be attributed to a number of factors. Perhaps most significantly is the fact that the samples were mounted in a fixed tilt holder. The tilt on the holder is intended to 'aim' the sample slightly toward the X-ray collector for the EDXS analyser, with the aim of permitting more X-rays to enter the collecting device.
However, this effectively places a limit to the number of grain boundaries that can be analysed, since analysis can only be performed on those that are exactly parallel to the axis of the sample holder. The use of a variable-tilt sample holder, such as the holder used in the FEGSTEM based at Harwell, would permit far more boundaries to be analysed, since they could have been perfectly oriented. This, in turn, would mean that a more accurate analysis could be performed, and therefore, statistically, a more valid result could be obtained.

As they stand, the grain boundary concentration results obtained from Liverpool facility can be expected to be much lower than the actual grain boundary concentration, owing primarily to the fact that few of the analysed boundaries were perfectly aligned owing to the lack of adjustment with the sample holder. An example of a particularly well aligned boundary is shown in Figure 4.8. It can be seen that the observed width of this boundary is two nanometres at the most. The analyses performed for the majority of the samples were not as accurate as this.

Additional errors in the results from Liverpool can be attributed to the short time available for analysis. Typically, it would take at least an hour to load a sample, and subsequently evacuate the specimen chamber to suitable vacuum conditions in the FEGSTEM. Where possible, samples were placed in the specimen holder the evening prior to being analysed. The reasons for this were to allow the sample to ‘settle’ in order to minimise any drift during analysis. Drift results in the analysis of regions of the sample other than the grain boundary, thereby diluting the actual element concentration measured.

It was found that less drift was observed after longer periods in the microscope. However, owing to the lack of perfectly oriented boundaries in samples, it was necessary to frequently change samples. In some situations, samples were loaded and would be analysed within an hour. During analyses, these samples typically exhibited significant drift. It was, however, possible to minimise this drift by performing careful analysis. A typical EDXS point analysis would take an overall collection time of around 250 seconds. During this time, the analysis could be stopped in order to check that the beam was still centred on the analysis area. Any sample drift could therefore be minimised. Even in samples exhibiting little or no drift, this procedure was taken as a precautionary measure.

The comparison of the experimental FEGSTEM results obtained from Liverpool and Harwell has highlighted several of the limitations associated with the technique. However, the major limitation of the technique is due to the finite size of electron beam that is employed. In Chapter 3, the advantages of the use of field emission gun electron sources over the more common tungsten wire and lanthium hexaboride sources were discussed. Even so, the FEGSTEM technique is still limited by the electron probe diameter. This effect can be illustrated by the diagram shown in Figure 9.1, which shows the current distribution of an electron probe on an imaginary grain boundary.
Figure 9.1: Geometry of the electron probe-grain boundary interaction (from Faulkner and co-workers\cite{34})

The analysis of any narrow interface would ideally be performed using an electron beam that is smaller than the width of the interface. However, a well oriented, low angle, grain boundary, such as that shown in the diagram, can be expected to be much less than one nanometre wide, or roughly three atomic planes. Even in the most advanced FEGSTEMs, the electron beam can be expected to be around 0.8 nanometres in diameter. Thus, the actual area of the beam is significantly larger than the width of the boundary being analysed. From the diagram, it can be seen that the X-ray emission would occur from both the grain boundary and the regions adjacent to the grain boundary. These emissions would effectively dilute the X-ray signal emitted from the grain boundary, and would reduce the observed concentration of elements.

The work of Faulkner and co-workers\cite{34} developed a method of correcting experimental results for these dilution effects. However, owing to the significant inaccuracies of the FEGSTEM results obtained from the Liverpool system, it has not been possible to perform these corrections. Likewise, the data from Harwell is insufficient to correct fully.

If the effects of electron beam broadening are considered, shown schematically in Figure 3.6, then the electron beam needs to be smaller, and the sample needs to be exceedingly thin. This aspect of microanalysis has been considered in detail by Faulkner and co-workers\cite{34}, who demonstrated that beam broadening was related to sample thickness by the power 3/2. In reality, the electron probe size will be a few nanometres in diameter. The effect of beam broadening can also be minimised, either by the use of higher electron beam currents, or by careful sample preparation. However, total elimination of beam broadening is hard to achieve.
9.1.3 AES analyses of grain boundaries

The use of AES to observe and measure grain boundary segregation has been used by many of the research groups whose work has been discussed in relation to thermally-induced segregation in Chapter 5. The technique has found favour owing to its relative ease of use and simplicity, together with the ease of sample preparation compared to those required for FEGSTEM analysis. Additionally, it is possible to accurately measure carbon concentrations. Within the scope of this work, a number of AES analyses have been performed on four of the post-weld heat-treated alloys.

The AES analysis of the samples returned values for the grain boundary concentrations of the elements phosphorus, molybdenum, carbon, nickel and copper, which were shown in Table 4.5. Perhaps the most significant aspect of the results is that there was very little intergranular fracture in the samples examined. This is somewhat surprising, considering the fact that the material was fractured in the AES apparatus after being cooled with liquid nitrogen. Additionally, the results from the FEGSTEM analyses performed prior to the AES analyses indicated that there should be phosphorus segregated to the grain boundaries, which should reduce the cohesiveness of the boundary regions, thereby promoting intergranular, brittle fracture. The AES analysis work was performed by experienced technicians, who commented that the predominantly intragranular fracture of such a material was unusual. In all, only fifteen suitably oriented and exposed grain boundaries were analysed. Analysis of these results can therefore only be qualitative, owing to the statistically small number of experimental observations that were obtained.

A summary of the AES results is shown in Table 9.2. These results express the mean enrichments of the elements, together with the standard deviations of the results. It can be seen that Alloy SL yielded insufficient suitably exposed grain boundaries to perform any statistical analysis. However, perhaps significantly, this alloy contains the lowest bulk phosphorus concentration of the four materials analysed. This could therefore very tentatively suggest that this particular alloy experiences very low phosphorus segregation, and therefore is less prone to brittle fracture than the other alloys. The one result that the sample did yield, however, was considerably lower than those obtained from the three other alloys, which would support this suggestion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P</th>
<th>Mo</th>
<th>C</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG100</td>
<td>43.0  (11.4)</td>
<td>6.8  (1.3)</td>
<td>84.0 (19.8)</td>
<td>3.1 (-)</td>
<td>3.4 (0.9)</td>
</tr>
<tr>
<td>SL387</td>
<td>30.0 (-)</td>
<td>1.8 (-)</td>
<td>- (-)</td>
<td>- (-)</td>
<td>- (-)</td>
</tr>
<tr>
<td>SP37</td>
<td>87.8 (9.8)</td>
<td>6.2 (0.2)</td>
<td>66.7 (5.5)</td>
<td>- (-)</td>
<td>- (-)</td>
</tr>
<tr>
<td>SF36</td>
<td>64.3 (18.3)</td>
<td>7.6 (2.3)</td>
<td>78.8 (11.4)</td>
<td>2.5 (-)</td>
<td>- (-)</td>
</tr>
</tbody>
</table>

Table 9.2: Mean GB enrichment ratios and (standard deviation)² of AES results

² Note: Standard deviations only calculated where 3 or more results were obtained
The highest phosphorus segregation is observed in alloy SP, which also has the lowest spread of the results. This can be seen by the low standard deviation in the results. However, this result is also surprising, since the samples from this alloy only yielded three suitable grain boundaries. Therefore, is this material more embrittled than alloy SG, owing to the higher phosphorus segregation, or is alloy SG more embrittled, since more grain boundaries were exposed during low temperature fracture? This question can only truly be answered by performing a detailed program of impact testing on the samples to investigate the brittle behaviour of the alloys.

The AES results from these alloys can be compared to those obtained from the FEGSTEM/EDXS analyses. In comparison to the results obtained from Liverpool, the results here indicate significantly higher phosphorus grain boundary segregation. However, comparison with the FEGSTEM/EDXS data obtained from Harwell shows a remarkably different trend. The figures from Harwell gave a mean enrichment ratio of 100 times bulk concentration for alloy SP, and 65 times bulk for alloy SG. In contrast, the AES results indicated enrichments of 88 times for alloy SP, and 43 times for alloy SG. It can be seen that the basic trend of these results is the same, where alloy SP has higher observed phosphorus concentrations than alloy SG.

Significantly, there was no manganese detected at the grain boundaries in the AES results, although enrichments of molybdenum, between 2 and 10 times bulk concentration, were recorded. Enrichments of copper were detected on exposed grain boundaries in alloy SG, which contains the highest bulk concentration of copper of the four alloys analysed. This behaviour is worth bearing in mind, and will be considered in more detail when discussing radiation induced segregation and precipitation behaviour of RPV steels. The results also indicate that a significant concentration of carbon is present at the grain boundaries in all the alloys bar alloy SL. However, since only one grain boundary was analysed in alloy SL, this result cannot be considered representative. This carbon segregation is to be expected since many precipitates were observed along the grain boundaries.

9.1.4 Limitations of AES analysis

As with FEGSTEM/EDXS, the technique of AES does, however, have limitations. The technique relies on the fact that materials fracture in a brittle, inter-granular manner when cooled, exposing grain boundaries in the process. In the work performed to characterise these alloys, it was found that even at low temperatures, the samples fractured in a predominantly transgranular manner, with very few grain boundaries exposed.

Additionally, the technique requires considerable experience to accurately identify grain boundaries on a fracture surface. Grain boundaries generally exhibit few identifying features. In many cases, the detection of higher concentrations of impurity and other solute elements are used to indicate that the area of analysis is in fact a grain boundary. Using this
assumption, if an exposed surface exhibits little or no significant segregation, then it is assumed that the surface is not a grain boundary. This situation is significant, since it would imply that the technique can only accurately measure grain boundary concentrations in highly embrittled materials, containing highly segregated elements. In those cases where the material is ductile, even when cooled, and contains low levels of grain boundary segregants, the technique cannot give an accurate and statistically significant result.

An additional limitation of the technique of the AES employed is that following sample fracture, only one half can be analysed, and cannot subsequently be re-analysed. Therefore, it has to be assumed that the segregation observed at the exposed half of the grain boundary is representative of the whole grain boundary. Lejcek and Hofman\textsuperscript{[167]} performed AES analyses on both fracture surfaces of an (001)/(011) asymmetrical grain boundary. A modified sample holder was used, which secured both ends of a standard 'matchstick' sample, which would enable comparison of both exposed fracture surfaces of the same grain boundaries. The sample observed was a 45° [100] tilt bi-crystal of an iron-silicon alloy, with small amounts of phosphorus and carbon present. A number of samples were prepared with the grain boundary perpendicular to the sample axis. The samples were then annealed at a range of temperatures to promote equilibrium segregation to the interface.

It was found that there was a significant difference between the two fracture surfaces. The concentrations of both phosphorus and carbon were both higher and the concentration of silicon lower on the (011) boundary than at the (001) boundary. This was in contrast to previously observed segregation at symmetrical grain boundaries in the same alloy, which was distributed evenly between both fracture surfaces\textsuperscript{[168]}. It was proposed that at asymmetrical boundaries, the distribution for available segregation sites was non-uniformly distributed about the 'core' of the boundary. Thus, there would be an uneven distribution of segregated elements between the fracture surfaces. This would also explain the difference in observed segregation between the phosphorus and silicon, owing to their repulsive interaction. Thus, phosphorus would cause any segregated silicon to remain at the opposite side of the grain boundary.

The ability to analyse two halves of a grain boundary is particularly interesting, and is an analysis technique that cannot be performed using FEGSTEM. The FEGSTEM analysis assumes that the grain boundary region is homogenous, and from the work of Lejcek and Hofman, it can clearly be seen that this is not the case.

\textbf{9.1.5 Alternative techniques to measure GB segregation}

The discussion has highlighted both the advantages and limitations of the use of FEGSTEM/EDXS and AES as techniques for determining grain boundary segregation, both in irradiated and thermally treated samples. It is clear that AES is suited to analysing brittle, highly segregated, thermally treated, materials. The apparatus required is also reasonably
priced. The use of FEGSTEM/EDXS is possibly one step above AES as a technique to accurately measure grain boundary segregation, since it can perform analyses on irradiated materials, and can more easily perform concentration profiles across interfaces. In addition, any types of alloy, not just embrittled, can be examined.

However, the limiting factors here are the electron probe size and, more importantly, the equipment cost. As has been shown, in order to accurately analyse a region of grain boundary that, typically, is assumed to be of the order of less than one nanometre wide, an electron probe that is less than this size is required. Ideally, segregation would be most accurately measured by using a technique that can identify individual atoms. One such technique is APFIM, and has been widely used, both to measure segregated layers\cite{36-38,107}, but also to identify and characterise ultra-fine grain boundary precipitates\cite{144,145}.

However, this technique also has limitations. Sample preparation is exceedingly difficult, owing to the needle-shape geometry of the samples. The likelihood of preparing a sample with a suitably oriented grain boundary located at the tip of such a sample is quite low. If a suitable sample is prepared, then the analysis of the grain boundary can be performed, and the atomic distribution of the various elements can be determined. This analysis, too, is limited, since the volume of material that is actually analysed at any one time is exceedingly small, typically of the order of a few hundred atoms. Therefore, it is necessary to perform a high number of analyses to obtain a statistically significant result.

As an alternative to the use of AES to measure segregation to grain boundaries, the technique of X-ray photoelectron spectroscopy has been investigated by Hallam and Wild\cite{169}. This technique is particularly suited to studying the chemistry of surfaces, but was limited by resolution. In this work, an improved XPS instrument, with a resolution of approximately 10\textmu m, was used to examine an iron-nickel alloy, with additions of tin and phosphorus. The alloy was part of a continuing study and the segregation of both phosphorus and tin had been well characterised previously by AES.

The results from the XPS analysis were found to be in close agreement to those obtained previously by AES. In addition, the analysis also indicated that both phosphorus and tin were segregated at the grain boundaries in their elemental states, and had not formed any compounds. However, the technique is still limited owing to its resolution, and as such, can only be used to analyse large grained material.
9.2 Discussion of theoretical modelling

It is hoped that it is now apparent that there are limitations to how accurate experimental results can be, and that there exists a need to be able to accurately predict the microstructural behaviour of the material on a finer scale than experimental techniques permit. In the following sections, the theoretical modelling of the RPV steel during post-weld heat treatments and subsequent reactor service life will be discussed. This will be followed by a brief discussion of the precipitation model that has also been investigated in this Thesis.

9.2.1 Modelling post-weld heat treatments

The models for thermally induced segregation have been used to predict the segregation of phosphorus, molybdenum, manganese and carbon during the simulated post-weld heat treatment that the RPV steel underwent. The heat treatment consisted of three phases that were designed to simulate the numerous stress-relieving processes that were actually used in the construction of the RPV. The first phase consisted of a water-spray quench from a temperature of 920°C. The overall cooling rate was calculated to be 146°C per hour to 300°C, and no intermediate cooling rates were quoted. This was followed by an initial temper at 600°C for approximately 42 hours, which was then followed by a shorter temper of 6 hours at a higher temperature of 650°C. The cooling rates after both tempers were considerably slower than that used in the initial phase. Following the first temper, the cooling rate was 23°C per hour, and following the second temper the cooling rate was only 38°C per hour.

In order to model the heat treatment using the thermally induced segregation models presented in Chapter 5, it was decided to model the first phase of the heat treatment using the non-equilibrium segregation theory. The subsequent isothermal tempers were modelled using both the binary equilibrium and ternary equilibrium co-segregation models. The predictions obtained from both models will be discussed here in relation to the experimental observations presented in Chapter 4. However, it must be noted that the experimental results that were obtained arise from the combined effects of the initial cooling process, together with the two subsequent tempering processes. Therefore, direct comparison of theoretical predictions with these observations is difficult, since no intermediate analysis of the samples has been able to be performed.

9.2.1.1 Comparison of model predictions with experimental observations

The first phase of the heat treatment was a water-spray cool from 920°C to 300°C at a rate of 146°C per hour. This was calculated to take over 4 hours. In order to model this situation using the TNES model, it was necessary to calculate an effective time for this quench. The model used was the basic approach of Song and Xu[82], which was further extended by Faulkner, Meade and Hales[84], which has been presented in Chapter 5. This
extended model determined the effective time of cooling processes, given the parameters of initial and final temperature, and overall cooling time. The exponential cooling curve for the initial water-spray quench produced by this approach was shown in Figure 5.34.

The model calculated that the effective quench time at the starting temperature of 920°C was approximately 200 seconds, using the input parameters shown in Table 5.13. In comparison, it was calculated that the critical effective time for desegregation at this temperature was considerably shorter at only 50 seconds. The TNES predictions would therefore be dominated by the desegregation mechanism. The prediction shown in Figure 5.35 for the segregation of phosphorus due to TNES was therefore calculated using this critical effective time, since this prediction would return the maximum theoretical level of segregation due to the cooling process. This prediction gave an enrichment factor at the grain boundary of less than 10 times the bulk concentration, with an enriched layer extending up to 3 microns into the adjacent matrix material. The solute depleted layer then extended a further 20 microns, with a minimum enrichment ratio of 0.1 times the bulk content. Converting these figures into atomic concentrations, the grain boundary concentration would be 0.4at.%, and the minimum figure for the depleted region corresponds to 0.004at.%.

Owing to the subsequent effects of desegregation, the segregation of phosphorus during the cooling process would be expected to be considerably less than this prediction. Unfortunately, the accuracy of this prediction cannot be compared to any available experimental data.

The final phases of the post-weld heat treatment process consist of isothermal tempering, firstly at 600°C for 42 hours and then for 6 hours at 650°C. Predictions for the segregation of phosphorus in a binary system for both temperatures are shown in Figure 5.27. It can be seen from these predictions that more phosphorus segregation is anticipated for longer tempering times, even at the lower temperature. After 42 hours at 600°C, the predictions indicate that phosphorus would become enriched to approximately 400 times the bulk figure. This figure equates to a grain boundary concentration of 16at.%, or approximately 0.6 monolayers, using the conversion of Beere40. At 650°C, following tempering for 6 hours, it is predicted that phosphorus is enriched to 300 times the bulk figure, equating to 12at.%. This figure converts to approximately 0.5 monolayers.

From these predictions, it can be assumed that the phosphorus segregation during the first temper is dominant. It could also be assumed that the effects of both tempers are cumulative, i.e. the phosphorus segregation after both processes can be expected to reach up to 700 times the bulk concentration. However, this maximum figure does not take into account any segregation or desegregation that may occur during the cooling processes that are used following the isothermal tempers. Likewise, these predictions do not account for the effects of other alloying elements.
The predictions from the ternary, co-segregation model show interesting trends. There has been considerable work published indicating that a number of alloying elements exhibit enhanced segregation in steels containing highly segregating non-metallic impurity elements, such as phosphorus. In particular, the interactions between phosphorus and molybdenum\cite{45,54,55,66,68} and phosphorus and manganese \cite{53,66,68} have received considerable attention. The interactions between phosphorus and both of these alloying elements have therefore been considered in modelling the tempering phases of the heat treatment.

The equilibrium grain boundary segregation predictions for phosphorus and molybdenum both in isolation, and interactively, have been presented. It was seen from Figure 5.28 that in isolation virtually no molybdenum grain boundary segregation predicted. However, when the model incorporates the previously published interaction parameter between the two elements\cite{68}, it can be seen that the predicted segregation of molybdenum increases dramatically. This prediction is shown in Figure 5.29., and indicates a molybdenum enrichment of approximately 10 times bulk content at an ageing temperature of 600°C after 42 hours.

Manganese and phosphorus interactions have also been considered in relation to the post-weld heat treatment. Again, their predicted segregation behaviours were calculated both independently, and interactively, using parameters published in the literature\cite{68}. However, it can be seen from Figures 5.30 and 5.31 that the predicted segregation of manganese does not significantly alter, unlike the segregation predictions for molybdenum. This can be attributed to the lower interaction parameter between phosphorus and manganese. However, at temperatures above 500°C, it would appear that this interaction would enhance the predicted grain boundary segregation of phosphorus.

From the AES analyses, the segregation of both phosphorus and molybdenum was observed at grain boundaries, whereas no manganese was detected. The figures indicated that phosphorus became enriched by a factor of approximately 100 times, and that the enrichment for molybdenum was up to 10 times. In contrast, the Liverpool FEGSTEM results indicated lower phosphorus segregation, but did detect both molybdenum and manganese at grain boundaries, again at low enrichments. However, the validity of these results has been questioned. The Harwell FEGSTEM results indicated phosphorus enrichments of up to 200 times the bulk concentration. Comparing these experimental figures with the theoretical results would indicate that the predicted phosphorus segregation is somewhat higher than the observed figure. However, the predictions for molybdenum and manganese would appear to be close to the observations. The deviations observed in the phosphorus results could be due to site competition with carbon.

Predictions for the grain boundary segregation of phosphorus and carbon, taking into account a site competition effect, are shown in Figures 5.32 and 5.33. These predictions assume carbon contents of 0.2 and 0.02at.% respectively. From these
predictions, it can be seen that lower carbon contents cause the predicted phosphorus segregation to increase at temperatures over 400°C, after an ageing period of 42 hours. However, the predictions for the carbon concentrations far exceed those observed in the AES analyses. This discrepancy can be attributed to inaccuracies in the AES analysis technique.

9.2.1.2 Discussion of the thermal equilibrium segregation models

The modelling approaches of McLean[63] and Guttmann[42,66,68] were used to obtain predictions for the thermal equilibrium segregation of phosphorus, together with its interactive segregation with the elements molybdenum and manganese. The discussion of associated literature presented in Chapter 5 highlighted some of the vast amount of work that has been aimed at accurately forecasting the grain boundary segregation of impurity elements during thermal heat treatments and service conditions. However, a large quantity of this work highlighted a significant aspect of the model, namely the diffusivity of the segregating elements. It has been shown in the supporting literature that the diffusivity of phosphorus varies depending upon the alloy through which it is diffusing. Therefore, in order to accurately model the segregation of phosphorus, it is necessary to obtain an appropriate value of the diffusion coefficient.

Grain boundary mis-orientation has been shown to influence segregation behaviour. In the early work of McLean[63] it was quoted that “The rate of segregation to a boundary should depend on the mis-orientation across the boundary”. The work of Lejcek and Hofman[167], discussed previously in relation to AES, highlighted the difference in segregation behaviour owing to grain boundary mis-orientation. Within the equilibrium segregation model, the mis-orientation is assumed to cause variation in the grain boundary width, which in turn is considered to influence the segregation kinetics. Therefore, to obtain more accurate model predictions, a range of grain boundary widths should be considered, which would give a range of results. Likewise, any experimental work should indicate the degree of mis-orientation of any analysed grain boundaries in order to more accurately compare with theoretical results.

Dislocations are not considered in the equilibrium segregation model. Again, from the early work of McLean[63], it was noted that “segregation to dislocations is quicker than to grain boundaries, partly because a dislocation is supplied from all sides, but mainly because it has a long range attraction for misfit solutes”. Clearly, this aspect of the model would require further work to determine its significance.

9.2.1.3 Discussion of the thermal non-equilibrium segregation model

It has been shown that the model for TNES is dependent upon the accurate determination of the effective quench time. The work presented in Chapter 5 highlighted a
new approach to more precisely modelling cooling curves assuming that they follow an exponential path. Previously, it had been assumed that cooling processes had followed a linear relationship between time and temperature. This exponential cooling process has been predicted using finite element heat transfer modelling of heat affected zone material in austenitic stainless steel\[^{84}\]. For comparison, the newly adopted approach to determining effective times returns predictions that are significantly shorter than those obtained from the previously used linear cooling assumption.

The predictions presented for segregation during cooling indicated that little or no segregation was expected, since the critical time for desegregation was exceeded. However, it is obvious that the rate of cooling of the material will vary with depth from the surface that is being cooled by sprayed water. It can therefore be expected that the surface of the material is cooled far more quickly than the core of the material. This, in turn, would mean that the predicted degree of segregation would vary with distance from the surface of the sample. Thus, at the surface, the material can be expected to be cooled to ambient temperatures far more quickly than the overall cooling time quoted, and therefore, the predictions obtained using the critical time for desegregation may actually more closely predict the segregation than previously thought.

The concentration profile adjacent to the grain boundary is also influenced by a number of factors. The work of Jiang and Faulkner\[^{86}\], upon which the model is based, effectively curve-fitted a previously assumed concentration profile. The profile predicted by the model of Jiang and Faulkner is based upon the calculation of the width of the solute concentrated layer, $w_{\text{sc}}$, shown in Figure 9.2. Subsequent calculations to determine the concentration at any distance, $x$, from the grain boundary incorporate this width. However, it was found that the width of the predicted enriched region using Equations 5.19(a) to (c) did not correspond to the calculated value of $w_{\text{sc}}$. Thus, the equations significantly over-predict the width of this enriched region.

![Figure 9.2: Comparison of TNES profiles](image-url)
A further limitation of this approach is the assumption of a depleted region, caused during the segregation process. The materials being considered in this work contain phosphorus concentrations of typically 0.04 at%. Defining a depleted region containing concentrations of less than this figure is therefore very difficult. This can be shown graphically in the EDXS spectra presented in Chapter 4. The spectra obtained from the matrix material would appear to exhibit only a slight 'peak' at the phosphorus energy level. Therefore, accurately defining what concentration exists, bearing in mind the background signal, is therefore difficult. In materials containing higher contents of alloying elements, such as the aluminium alloy for which the model was originally developed, a depleted region can be more easily determined experimentally.

9.2.1.4 Atomistic simulation of thermally induced segregation

The atomistic simulation presented in Chapter 8 could be argued to model microstructural processes more precisely than the analytically based models that have just been discussed. The model predicts the random movement of both impurity atoms and vacancies, solely on the basis of their binding energy data. This approach to modelling therefore is considerably simpler than the Monte Carlo simulations that have been used to predict neutron-induced damage cascades[16,17], which consider the behaviour of all of the species in the matrix.

The simulations presented in Figures 8.2 and 8.3 predicted that segregation of boron in a simple cubic lattice would occur after very short times at high temperature. The simulations indicated that after 2 milli-seconds, there was significant grain boundary enrichment. In addition, it can be seen that the vacancy concentration adjacent to the grain boundary is significantly lower than that further from the boundary. This would indicate that the model predicts rapid vacancy migration to the boundary. Additionally, the model includes a continual flux of vacancies entering the matrix, which would explain the higher concentration of vacancies further away from the boundary. In comparison to the boron, phosphorus did not appear to segregate greatly in the simulation shown in Figures 8.6 and 8.7, which represent 10 milli-seconds of real time.

Since the model considers the segregation of elements at high temperatures, the model can be compared to the analytical model of TNES, since this model also assumes that segregation occurs at high temperatures over short time periods. It could be proposed that the atomic simulation of phosphorus agrees with the analytical TNES predictions for phosphorus segregation following the first cooling process of the heat treatment. These TNES predictions, shown in Figure 5.31, predicted that the critical time for desegregation was 47 seconds at a constant temperature of 920°C, and that the grain boundary concentration was only slightly enriched. In the atomistic simulation, which was performed
for a 'real' time of 10msec, it could be seen that there was very little grain boundary segregation of phosphorus.

For comparison, the phosphorus predictions obtained from the analytical TNES model for an effective time of 10msec are shown in Figure 9.3. It can be seen from the predictions that even after such a short time, the TNES model predicts significantly more grain boundary segregation than the atomistic model. This difference in the predictions can be attributed to a number of 'features' of the analytical model, as well as to the relative simplicity of the atomistic model. The TNES model assumes that the concentration at the grain boundary of the segregating element is reached instantaneously. Recalling Equation 5.12, this concentration is related purely to the temperature at which the calculations are performed. Thus, for a cooling process, such as that considered in the RPV heat treatment, the start temperature of the quench governs the grain boundary concentration. In the kinetic modelling of TNES, the width of both the solute concentrated layer and the solute depleted layer increase with time, up to the critical desegregation time. There is no allowance made for the grain boundary concentration to gradually build up with time, which would appear to be the more logical scenario. This behaviour is considered more realistically in the atomistic simulations, and has been observed in the simulation of boron.

![Figure 9.3: Predicted TNES concentration profile for phosphorus after 10msec at 920°C](image)
However, a major limiting factor of the atomistic simulation is that it assumes that the segregating element is migrating simply by atomic exchange with its nearest neighbours. Although attractive interactions between impurities and vacancies are considered, there appears to be no clustering observed in any of the simulations that were performed. Likewise, the formation and migration of nearest neighbour complexes of vacancies and segregating elements does not appear to occur in any of the simulations. This is perhaps the most significant difference between these simulations and the analytical TNES model, which assumes that segregation occurs by complex migration alone, since the diffusivity of the complexes is calculated to be quicker than that of the individual solute element.

In order to accurately account for the migration of nearest neighbour complexes within the atomic simulation, the model would need considerable alteration, and would therefore lose its relative simplicity, which could be argued to be its main advantage. Vacancy-solute atom complex migration, as shown in Figures 5.21 and 5.22 is assumed to occur in three dimensions. The atomic simulation has therefore been extended to consider a simple cubic structure in three dimensions, and the predictions obtained for boron segregation are shown in Figures 8.8 and 8.9. These results indicate similar behaviour to the two-dimensional model, although the computing time required to perform the simulations increases dramatically, since more calculation time is required per simulation cycle.

To more accurately simulate three-dimensional segregation, the model was further modified to consider both body centred cubic and face centred cubic crystal lattices. Again, the simulated grain boundary segregation of boron was similar to that predicted by the two-dimensional model, although the simulation had to be performed for considerably more calculation cycles. This effectively simulates a longer real time situation. However, having extended the simulation to consider migration through realistic crystal lattices, it was found that the predictions obtained were taking considerable time to perform.

9.2.2 Modelling segregation during reactor service life

The embrittlement of RPV steels is a major concern to operators of nuclear reactors. Catastrophic failure of any reactor component, generally due to brittle fracture of materials, cannot be tolerated. The accurate forecasting of the service lifetime of reactor components and RPV's is therefore sought after. The work presented in Chapter 6 extended an analytical model to more realistically predict segregation of solute elements in ternary steel alloys, during continued irradiation. The predictions of these models will be discussed, and compared with experimental observations of segregation obtained using the micro-analytical technique of FEGSTEM/EDXS, which were presented in Chapter 4. The extended theoretical model itself will be discussed in some detail, highlighting the improvements over previous models, together with a discussion of its limitations.
9.2.2.1 Comparison of model predictions with experimental observations

During continued irradiation, there is a continual production of point defects. These defects, both vacancies and self-interstitial atoms, can interact with solute elements, and migrate through the matrix owing to the concentration gradient of each species adjacent to sink regions. It is now generally accepted that the mechanism of segregation of undersized solute atoms is that of long range migration toward interstitial sinks by self-interstitial atom-undersized solute atom bound complexes. A theoretical comparison of this mechanism of segregation, and that of vacancy-solute atom complex diffusion, has been shown in Figure 6.20, for phosphorus as the solute element. It can be seen that the predictions are dominated by the segregation of SIA-undersized solute atom complex mechanism. At an irradiation temperature of 200°C, this mechanism of segregation gives predictions that are almost 3 orders of magnitude higher than that of the vacancy-solute atom complex. This difference diminishes up to around 320°C, where the predicted grain boundary enrichment begins to fall, and the higher temperature effect of irradiation-enhanced equilibrium segregation being to dominate the predictions. At typical reactor operating temperatures, between 255 and 315°C, it is predicted that the SIA-undersized solute atom mechanism would cause the enrichment of phosphorus at grain boundaries to be approximately 60 000 times the bulk concentration. In more meaningful terms, this equates to a grain boundary concentration of 1200at.%, assuming an initial bulk concentration of 0.02at.%. This figure is obviously unrealistic, since 1 monolayer of phosphorus has been determined to be equal to only 25at.%. This dramatic overprediction of the model can be accounted for by the fact that the model only considers segregation in binary alloy systems, i.e., phosphorus segregating in isolation in an iron matrix.

The microstructural parameters of grain size and dislocation density have been accounted for within the binary segregation model. Grain size can be seen to significantly influence the predictions, as shown in Figure 6.21. At lower irradiation temperatures, where the segregation mechanism is dominated by radiation induced segregation, it can be seen that larger grain sizes induce higher predictions of grain boundary segregation. This is due to the larger total supply of solute atoms that are present in larger grained material.

The effect of dislocation density variations on the binary model predictions are shown in Figure 6.22. It can be seen that the effect of dislocation density on the predictions is most significant where the temperature is between 200°C and 400°C. At temperatures that lie within this range, the increasing dislocation density causes less grain boundary segregation. This is due to the increase in dislocation sink strength at higher densities, which causes less solute to be able to segregate to grain boundaries.

The influence of the irradiation conditions of dose rate and dose on the predicted segregation can be seen in Figures 6.23 and 6.24. Increasing the dose rate from $10^{-12}$ to $10^{-8}$ dpa/s causes the peak segregation level to be maintained over a larger temperature
range. Increasing the dose for a given dose rate can simply be achieved by increasing the duration of the irradiation. Therefore, it can be expected that more irradiation enhanced equilibrium segregation can occur. This effect can be seen in Figure 6.24.

The inclusion of a grain boundary site competition effect between phosphorus and carbon dramatically alters the predicted phosphorus segregation. The modelling approach makes the assumptions that, firstly, the two elements segregate to the grain boundaries independently. Secondly, once at the grain boundary, the elements can re-distribute in proportion to both their concentrations, and their grain boundary binding energies. These assumptions do, however, simplify the situation somewhat. By assuming that the elements can segregate independently, any interaction between segregating complexes is ignored. Similarly, assuming that the redistribution at the grain boundary is related to the bulk concentration of the two elements eliminates the influence that segregation may have on the grain boundary concentration. However, since there is no available data for the carbon concentration at grain boundaries in RPV steels due to irradiation, this assumption has to be assumed to be valid.

The effect of the irradiation conditions and the microstructural parameters of dislocation density and grain size are shown in Figures 6.25 to 6.28. These predictions include irradiation enhanced equilibrium segregation, which occurs at higher temperatures. In comparison to the predictions of the binary model, it would appear that considerably less phosphorus segregation is anticipated. This is due to the site competition effect with carbon at the grain boundary. In these predictions, it can be seen that the peak enrichment ratio is expected to be around 100 times the bulk content. This figure corresponds to an actual concentration of around 4 at.%, or roughly 20 percent of a monolayer.

Figures 6.29 through to 6.33 show the predictions for each of the alloys that have experimental data. These figures indicate the predictions of both the binary model, and the newly extended ternary model, together with the experimentally obtained figure. The predictions of the ternary model have been obtained using both the carbon bulk content, together with a carbon concentration of one tenth of this figure. The lower carbon concentration can be assumed to more accurately represent the concentration of carbon that is in solution in the alloy, and that can participate in segregation to grain boundaries.

The predictions indicate far closer agreement to the experimental observations than the predictions obtained from the ternary model. The prediction for alloy SL, shown in Figure 6.33, would appear to be the only prediction that underpredicts the observed segregation. However, this material was irradiated at a slightly higher temperature than the other samples, which could be the main reason for error. Additionally, it is worth considering the fact that experimental observations of samples SP65 and SG35 indicated that there was no further enrichment of phosphorus at the grain boundaries compared to the post-weld heat treated samples. The error bars shown on the graphs indicate the spread of the results.
However, the ternary model still returns predictions that are within an order of magnitude of these observations, which is considerable improved over the predictions of the binary model.

Combining the experimental data from the Rolls Royce and Associates with data taken from Magnox carbon-manganese RPV steels, it is possible to produce a summary graph of grain boundary enrichment of phosphorus as a function of irradiation temperature. This can be seen in Figure 9.4. Although this graph is very simplified, it does indicate that at most, the observed grain boundary segregation of phosphorus due purely to irradiation does not exceed an enrichment factor of 200 times the bulk content.

Returning to the ternary model predictions shown in Figures 6.29 to 6.33, it can be seen that the peak enrichment factors predicted for the alloys is of the order of 100 times bulk content. This is comparison to the binary model predictions of approaching 10000 times the bulk content. Even considering the range of dose rates that the materials have been subjected to, from $10^{-8}$ to $10^{-12}$ dpa/s, the ternary model predictions, shown in Figure 6.26, indicate again that the peak enrichment would rarely exceed 100 times bulk content.

The irradiation doses that the materials have been subjected to also vary, although only between 1 and 40mdpa. From Figure 6.27, it can be seen again that the ternary model of segregation only returns a peak enrichments of around 100 times even after varying the irradiation dose by two orders of magnitude.

![Figure 9.4: Irradiation induced enrichments of available RPV steel data](image)

3 The Magnox carbon-manganese RPV steels typically contain between 0.03 and 0.05 at.% of phosphorus. Exact grain sizes are not known, although it is known that the dislocation densities range from $5 \times 10^{13}$ to $1.5 \times 10^{14}$ m$^{-2}$.
where:

a is AES data from Beere\(^{[40]}\), dose = 2.287-2.656mdpa, dose rate = 1.7-3.3 \(\times 10^{-12}\) dpa/s
b is AES data from Beere\(^{[40]}\), dose = 1.055-1.862mdpa, dose rate = 3.4-4\(\times 10^{-12}\) dpa/s
c is AES data from Beere\(^{[40]}\), dose = 1.929mdpa, dose rate = 3\(\times 10^{-12}\) dpa/s
d is FEGSTEM data from Druce\(^{[170]}\), dose = 0.94mdpa, dose rate = 1\(\times 10^{-12}\) dpa/s
e is FEGSTEM data from Druce\(^{[170]}\), dose = 9.2mdpa, dose rate = 10\(^{-9}\) dpa/s
f is AES data from Druce\(^{[170]}\), dose = 9.2mdpa, dose rate = 10\(^{-9}\) dpa/s
g is AES data from Druce\(^{[170]}\), dose = 9.5mdpa, dose rate = 10\(^{-9}\) dpa/s
h is FEGSTEM data from Druce\(^{[170]}\), dose = 1.52mdpa, dose rate = 10\(^{-12}\) dpa/s
i is FEGSTEM data from Druce\(^{[170]}\), dose = 8.61mdpa, dose rate = 10\(^{-9}\) dpa/s
j is FEGSTEM data from Druce\(^{[170]}\), dose = 9.11mdpa, dose rate = 10\(^{-9}\) dpa/s
k is FEGSTEM data for Sample SG25, dose = 1.5mdpa, dose rate = 8.9\(\times 10^{-11}\) dpa/s
l is FEGSTEM data for Sample SG02, dose = 12.34mdpa, dose rate = 6.4\(\times 10^{-10}\) dpa/s
m is FEGSTEM data for Sample SG35, dose = 29mdpa, dose rate = 6\(\times 10^{-9}\) dpa/s
n is FEGSTEM data for Sample SP65, dose = 38mdpa, dose rate = 6\(\times 10^{-9}\) dpa/s
o is FEGSTEM data for Sample SL125, dose = 26.62mdpa, dose rate = 6.3\(\times 10^{-9}\) dpa/s
p is FEGSTEM data from Song\(^{[90]}\), dose = 0.042dpa, dose rate = 1.05\(\times 10^{-6}\) dpa/s
q is FEGSTEM data from Song\(^{[90]}\), dose = 0.13dpa, dose rate = 1.75\(\times 10^{-8}\) dpa/s

9.2.2.2 Discussion of the limitations of the radiation induced segregation model

The modelling of the post-weld heat treatment, using thermal equilibrium segregation models, considered the effects of interactive co-segregation between the impurity element phosphorus, and the metallic alloying elements of molybdenum and manganese. Using published parameters for the interaction coefficients, the predicted segregation behaviour of the three elements was calculated. It was shown theoretically that molybdenum would segregate more due to its interaction with phosphorus, whereas manganese would be little affected.

Modelling a similar phenomenon during irradiation is more difficult, however. The mechanism of segregation during irradiation is that of SIA-undersized solute atom complex migration. It is entirely justifiable to assume that some form of co-segregation takes place between certain alloying elements during irradiation. However, incorporating these effects into the RIS mechanism is more difficult, since the mechanism of segregation would need to be altered to allow for the two co-segregating elements.

The predictions presented have only considered one grain boundary width. It has been assumed that a width of 1\(\text{nm}\) is representative of a typical grain boundary. However,

\^4 The material analysed by Song was a 2\(\frac{1}{4}\)Cr1Mo steel
this figure should be higher for highly mis-oriented grain boundaries. This would increase the number of sites available for segregation, and therefore more segregation would be predicted. However, since the effect of grain boundary misorientation is overlooked in the experimental results, no comparison can be made here.

The dislocation density is included in the modelling of radiation induced segregation, owing to its behaviour as a sink for both vacancies and interstitials. However, the figure used in the modelling predictions assumes a uniform distribution of dislocations throughout the material. The micrograph shown in Figure 4.9 shows how non-uniform the distribution of dislocations can be. The figure shows a pile-up of dislocations adjacent to a grain boundary precipitate. These dislocations would be expected to act as sinks for the material surrounding them. However, dislocations are also fast diffusion paths for some elements, and therefore these dislocations could supply solute atoms to the grain boundary. Again, this highlights the fact that the model can only predict a mean figure for segregation, and that upper and lower bounds to the parameters should be considered.

9.2.2.3 Discussion of the radiation-enhanced equilibrium segregation model

The model presented in Chapter 6 for the segregation of phosphorus in a ternary alloy system containing carbon also considered the irradiation-enhanced equilibrium segregation of phosphorus. The model assumed that radiation enhanced the diffusivity of segregating substitutional elements, owing to the continual formation of isolated point defects within the matrix of the material. The predicted increase in phosphorus diffusivity is limited to low temperatures, typically below 400°C, as shown in Figure 6.17. At higher irradiation temperatures, it can be seen that the diffusivity of phosphorus remains equal to its thermal diffusivity.

The predictions for total radiation induced segregation indicate that the effect of radiation enhanced equilibrium segregation becomes dominant at higher irradiation temperatures, typically at temperatures exceeding 300-350°C, even though the diffusivity is enhanced at lower temperatures. The model predictions obtained for alloy SL, presented in Figure 6.33, show that at the actual irradiation temperature of 315°C, the mechanism of segregation would appear to be in transition. The predictions at this temperature lie somewhere between the lower temperature mechanism of radiation induced segregation by SIA-impurity atom complexes and the mechanism of irradiation enhanced equilibrium segregation.

This model could be extended in a number of ways. Possibly the most important area would be to investigate co-segregation effects. Experimentally, it has been shown that during thermally-induced equilibrium segregation, the segregation of molybdenum is enhanced due to the segregation of phosphorus. Owing to the enhancement of phosphorus
segregation at low temperatures due to irradiation, a further enhancement of irradiation enhanced equilibrium segregation of molybdenum could be expected.

9.2.2.4 Inverse Kirkendall segregation and Rate Theory modelling

The modelling of segregation by Inverse Kirkendall effects and Rate Theory models has received considerable attention by a number of workers\cite{91,124,172,174}. The approach considers the simultaneous diffusion of a number of segregating species, both toward and away from grain boundaries. The majority of the work published has been aimed at determining segregation within austenitic stainless steels, although recently work has been performed aimed at predicting irradiation induced segregation within ferritic matrices. It has been shown in the literature that the model can be applied to both thermally-induced non-equilibrium segregation and irradiation-induced segregation, in both dilute and concentrated alloy systems.

Since no work has been performed within the scope of this Thesis to investigate Rate Theory modelling, discussion of the modelling technique in light of the experimentally observed results is difficult. However, Rate Theory modelling work performed by English and Agnew\cite{124} investigated the segregation of phosphorus in a bcc matrix. This work has been highlighted in Chapter 6. A discussion of these results will be presented here.

The predictions obtained from the model, shown in Figures 6.11 and 6.12 indicated that at an irradiation temperature of between 250 and 300°C, the grain boundary coverage of phosphorus is predicted to be 25at.%. This figure has been obtained assuming a phosphorus bulk concentration of 0.005wt.%. However, the model considers the grain boundary concentration prior to irradiation. In the case of the predictions shown, it can be seen that prior to irradiation, it was assumed that the grain boundary coverage of phosphorus was 20%. Therefore, the effect of irradiation can be considered to be the difference between the two figures, i.e. an increase in coverage from 20% to 25%. However, without more details of the exact modelling procedure, the significance of this cannot be interpreted.

The results presented from English and Agnew also consider the effect of dislocations on the grain boundary segregation. Dislocations have been shown to have a dramatic influence on a number of irradiation induced phenomena\cite{175}. Dislocations can act as sinks for migrating vacancies and interstitials, which therefore reduces the quantity of these species which can segregate to grain boundaries. Additionally, it has been shown that point defects created by irradiation can cluster to form additional dislocations, which in turn can remove a larger quantity of freely migrating defects from the material, lowering the grain boundary segregation further.

However, there are still features of the analytical model that are overlooked in the Rate Theory modelling approach. In the analytical models used in this work, the grain size is
used to determine the critical times for either desegregation, in the case of thermal non-equilibrium segregation, or steady state segregation, in the case of irradiation induced segregation. These assumptions can be justified, since there exist only a finite quantity of solute elements in the material that can participate in segregation. Thus, larger grained material would contain a larger quantity of solute that could segregate. Likewise, smaller grained material would contain proportionally less solute that could contribute to grain boundary enrichment. These considerations have not yet been fully considered in the Rate Theory modelling approach.

Additionally, the width of the grain boundary has been overlooked. This parameter is of importance, since high angle boundaries will have a larger degree of mis-orientation. Therefore, these boundaries will be wider than low angle boundaries (an example is shown schematically in Figure 2.5), resulting in more sites for segregating atoms. In the solute drag model described in this Thesis, the width of the grain boundary in incorporated into the kinetics of the process. This is one area that could be investigated in future should further work in Rate Theory modelling be performed.

9.2.3 Precipitation modelling

An extended model of grain boundary precipitate nucleation and growth during ageing was presented in Chapter 7. The model was used to obtain predictions for carbide growth in an austenitic stainless steel used in the un-irradiated steam circuitry of power generating reactors. The following sections will discuss the theoretical predictions in comparison with the experimentally observed precipitate growth. In light of this discussion, the merits and limitations of the theoretical model will be considered.

9.2.3.1 Comparison of model predictions with experimental observations

The modelling that has been performed to predict the nucleation and growth behaviour of Cr23C6 precipitates in a Type 316 stainless steel matrix is possibly the first work that has given predictions for such extended periods. Previously, predictions have been presented using theoretical models that have considered only short time periods, such as those used for many heat treatments. Take, for example, the theoretical model of Jiang and Faulkner, upon which the current model is based. The work predicted precipitation behaviour in aluminium alloys, isothermally aged for periods of up to a few hundred minutes. Prior to Jiang and Faulkner, Carolan and Faulkner presented predictions for the behaviour of M23C6 precipitation in Alloy 800, for periods up to 1000 minutes. The growth of M23C6 particles in Nimonic PE16, treated theoretically by Faulkner and Caisley, only considered ageing times of between 15 and 3600 seconds.

The application of the model in this work was aimed at obtaining realistic precipitate predictions for the total service life of an austenitic stainless steel used in an electrical power
generating reactor. The experimental measurements of the precipitate sizes in the alloys were taken from a number of micrographs, such as those shown in Figures 7.11 to 7.16. These SEM micrographs show grain boundaries of the steel at a range of magnifications.

Comparisons of the theoretical predictions with the experimental observations of precipitation in the three alloy systems considered are shown in Figures 7.18 to 7.20, for service times of up to 100 000 hours. It can be seen that the average observed radii of the precipitates are typically in the order of tens of nanometres. However, the error bars on the experimental results indicate some precipitates with radii as small as a few nanometres, and other precipitates growing to several hundred nanometres. It would appear that the theoretical model is, in general, predicting precipitate sizes that are well within the error bars of these experimental observations.

The predictions for alloys AM and AK, shown in Figures 7.18 and 7.20, show the closest agreement with the experimental measurements. These predictions indicate that the theoretical precipitate growth at the experimental data point is due to the third growth mechanism, termed coarsening. During coarsening, the total volume of precipitate in the material remains constant, whilst the number of precipitates falls, corresponding to an increase in the average precipitate size. Prior to this coarsening mechanism, the model would appear to predict that the growth rate of the precipitates due to coalescence had reached almost zero. However following the onset of the coarsening mechanism, the predicted precipitate size increases rapidly, before reaching an almost steady size.

For both shorter service times and lower temperatures, there would appear to be some deviation of the theoretical predictions from the experimental observations. This is illustrated with the predictions for Alloy QP, shown in Figure 7.19. Experimental measurements of the precipitate sizes in this alloy, aged at 550 and 500°C, were performed at approximately 4000 and 60 000 hours, showing mean radii of 68nm and 50nm, respectively. However, the theoretical predictions appear to be significantly lower than these measurements. At 550°C, after 4000 hours, the theoretical prediction is only 10nm. Likewise, at 500°C, after 60000 hours, the model returns a similar size. This would indicate that either the particle has grown more rapidly at the early growth stages, or that the nucleation sizes of the particles are larger than those predicted in the model.

9.2.3.2 Discussion of the modelling approach

It has been shown that there are limitations of this model. In particular, the under-prediction of the precipitate behaviour for the material aged both at lower temperatures and shorter times highlights a shortcoming of the model. However, this under-prediction could possibly be explained by the calculation for the onset time of the mechanism of particle coarsening. The equation to determine this critical time (Equation 7.31) is related to both the grain size of the material and the diffusion coefficient of the solute element at the service
temperature. This latter parameter has been well documented. However, the exact range of grain sizes for the alloys under consideration were not known, and so a representative figure of 50 microns was assumed in the calculations. Using smaller grain sizes in the model would cause the critical time for coarsening to decrease quite dramatically. It may therefore be the case that the grain size of the material was less than 50 microns, causing the critical time for the onset of coarsening to be overestimated. Further experimental data would be required to verify this limiting factor.

A feature of the model was the inclusion of the effect of thermal non-equilibrium segregation of chromium. It was anticipated that the any chromium segregation to grain boundaries would enhance the rate of growth of grain boundary precipitates. Likewise, it was expected that the solute depleted region predicted in the TNES model would also influence the rate of precipitate growth at later stages owing to the diffusion distance of the solute atoms to correspond to the distance of the solute depleted region. However, the segregation model predicted that the magnitude of chromium enrichment at the grain boundary was only a few times that of the bulk material. Additionally, it was predicted that the predicted width of the solute concentrated layer of chromium adjacent to the grain boundary extended several thousand nanometres into the matrix. The chromium concentration immediately adjacent to the grain boundary was therefore almost constant. The combination of these two factors reduces the effect that grain boundary segregation has on the predicted growth rate of the precipitate. Were the concentration profile considerably narrower, as was predicted in the original model for aluminium alloys, then the predicted precipitate growth rate would be influenced more dramatically.

9.2.3.3 Precipitation during irradiation

The model developed in this work considered the effect of thermal non-equilibrium segregation of chromium on the precipitation behaviour of Cr$_2$C$_6$ in thermally aged austenitic stainless steel matrix. This segregation is caused purely by the thermal effects of quenching, causing non-equilibrium conditions, and subsequent ageing, which causes the solute depleted region to slowly return to matrix concentration. It has been shown that the model can be applied to obtain realistic predictions for material that is used in the secondary steam circuits of nuclear reactors.

The predictions presented in this work have assumed that chromium has been enriched at the grain boundaries, owing to thermal non-equilibrium segregation. This, in turn, has slightly accelerated the growth of the grain boundary precipitates, owing to the localised solute enrichment adjacent to the grain boundary. However, chromium has been observed to become depleted at grain boundaries in austenitic stainless steels during prolonged irradiation[21,95,142,175,177]. It can therefore be asked, what influence would this
depletion of chromium have on the growth of \( \text{Cr}_{23}\text{C}_6 \) precipitates in austenitic stainless steels during prolonged irradiation?

Logically, it would be expected that the desegregation of chromium during irradiation would slow the rate at which these precipitates grow. However, this depletion of chromium at grain boundaries has been found to be localised to a few nanometres on either side of the grain boundary. Therefore, would this cause a dramatic change in the precipitation behaviour? Further modelling and experimental work would be needed to investigate this behaviour.

Additionally, observations of ultra-fine copper precipitates have been made in a number of irradiated ferritic RPV steels\(^{145} \). These precipitates are typically a few atoms in size, and have been observed using the techniques of APFIM and three-dimensional PoSAPFIM. It was also found that phosphorus was segregated at the interfaces of these copper clusters. In addition, Miller and Burke\(^{38} \) observed phosphorus clusters in A302B steel, as well as molybdenum phosphides in A533B steel, and copper phosphides in an Fe-Ni-Cu-P model alloy. It would therefore be interesting to consider the application of some form of precipitation model to predict the behaviour of these precipitate phases.
Chapter 10: Conclusions and further work

The work presented in this Thesis represents three years work studying and modelling the varied phenomena that occur in a range of structural steels, due to post-weld heat treatments, long term service, and to continual irradiation during reactor service life. The work has concentrated primarily on the modelling of grain boundary segregation, and in particular, the segregation of phosphorus, in ferritic RPV steels. The material considered for this aspect of the work was material taken from a longitudinal seam weld in the pressure vessel, performed using the technique of submerged arc welding. In addition, the long term thermally induced precipitation behaviour of austenitic stainless steel has been considered, owing to the widespread use of this technological alloy in many power station applications.

The modelling of the post-weld heat treatment has been considered using theoretical models for thermally induced equilibrium and non-equilibrium segregation. The newly improved model of thermal non-equilibrium segregation predicted that following the first, high temperature, phase of the heat treatment, little grain boundary segregation of phosphorus would be expected. However, during the subsequent isothermal heat treatments, performed at lower temperatures, considerable equilibrium phosphorus segregation was predicted by the models. This predicted segregation behaviour was also shown to enhance that of molybdenum, without any significant influence on that of manganese. These predictions are in agreement with work published in the literature. However, compared to the experimental observations performed by the techniques of FEGSTEM/EDXS and AES, the models would appear to overpredict the behaviour of the phosphorus and carbon, although the manganese and molybdenum predictions are closer. The experimental observations that were obtained from the AES analyses were very limited, and statistically cannot be interpreted reliably. Similarly, the FEGSTEM/EDXS analyses performed at Liverpool were severely limited. The only accurate data for phosphorus segregation was obtained from the Harwell work. However, this work returned no data for segregation of the elements manganese and molybdenum.

Thermally induced segregation has also been considered using an atomistic simulation approach. This simulation has been extended considerably to more accurately model the structure of metals, and the predictions were compared with those of the thermal non-equilibrium segregation model. It was found, however, that there was a considerable difference in the predictions obtained. This difference was attributed to the assumption used in the analytical model which considers that enrichment at the grain boundary occurs instantaneously. In the atomistic simulation, it could be seen that the enrichment of solute builds up over time. In addition, the mechanism of segregation in both models is subtly different, with the analytical model assuming vacancy-solute complexes, and the atomistic simulation only considering atomic jumps.
The predictions of the radiation induced segregation model have been improved dramatically, owing to consideration of the effects of carbon on the segregation behaviour of phosphorus. The model now incorporates the effect of grain boundary site competition between these two segregating elements, which has been shown in the literature to be a significant effect. The predictions obtained from this newly improved model show much closer agreement to the experimentally observed figures than the previously used binary model, which considered the segregation of phosphorus in isolation. The model was shown to be sensitive to changes in dose rate, dislocation density and grain size, with dose only affecting the predictions at higher temperatures. In all cases, it was found that the maximum enrichment was of the order of hundreds of times the bulk content, compared to the predictions returned from the binary model which indicated enrichments of thousands of times the bulk content.

The radiation induced segregation model also considers the simultaneous effect of irradiation enhanced equilibrium segregation. The predictions show that this mechanism of segregation becomes dominant at higher irradiation temperatures. It was found, however, that at the predicted transition temperature between radiation induced segregation and irradiation enhanced equilibrium segregation, the predictions from the model slightly underestimated the experimentally observed segregation.

Long term predictions of Cr$_3$C$_2$ precipitation growth in an austenitic stainless steel have also been obtained from a newly improved model. These predictions consider the nucleation, coalescence and coarsening of precipitates using an iterative model. The model also incorporates the effect of the grain boundary segregation of chromium, both during quenching from high temperature solution treatment, and during service life. The experimental observations of actual precipitate behaviour indicated that the model is closely predicting the phenomenon, although at lower temperatures and shorter ageing times, there appear to be some inaccuracies.

There are a number of possible avenues of future work. Experimentally, it would be advantageous to perform a more detailed microstructural examination of the RPV steel, at various stages of the heat treatment. The data obtained from these analyses could be used to verify the predictions obtained from the thermally induced segregation models that were used and extended in this work. This experimental work could be performed using the technique of AES, although FEGSTEM would be preferable owing to its ability to determine segregation adjacent to grain boundaries more accurately and easily.

Examination of irradiated RPV steel using the technique of APFIM would also provide valuable data relating to the ultra-fine precipitation behaviour of copper and phosphorus that has been observed in similar material presented in the literature. This data could be used in comparison with currently available impact strength data to determine a correlation between grain boundary segregation, grain boundary precipitation and irradiation
induced hardening and embrittlement. This could subsequently be used to determine which of the mechanisms is more significant in influencing the material properties.

Theoretically, there are a number of areas of future work that could be suggested. The thermal non-equilibrium segregation model could be developed to quantify the grain boundary concentration of segregating elements more accurately, by considering the rate at which the concentration will build up. This would avoid the current situation that predicts that the grain boundary enrichment occurs instantaneously, and remains constant up until the critical desegregation time, a situation that is clearly unrealistic. The model could be also be improved to predict the segregation behaviour of ternary systems, such as by considering a site competition effect between phosphorus and carbon. This would permit more accurate forecasting of segregation during post-weld heat treatments.

In order to fully develop this model, sufficient experimental data would be required in order to validate the modifications. The use of FEGSTEM/EDXS to quantify the concentration profiles adjacent to the grain boundaries would also aid the modification of the model to more accurately forecast enriched and depleted regions. This aspect of the model currently requires some modifications, since it would appear to dramatically over-predict the actual widths of these regions. Likewise, the assumption that a depleted region of solute exists in alloys were the segregating species is only present in very small quantities needs more consideration.

Following on from the work that considers the cooling of a material, the TNES model could be developed to consider segregation iteratively, in a similar manner to the model presented earlier for long-term precipitation. The cooling process could therefore be modelled more accurately, since the segregation during each incremental time interval would be predicted, and would be summed to obtain an overall segregation figure. Should this approach be adopted, it may then be possible to incorporate certain aspects of the precipitation model, which currently assumes that precipitate nucleation only occurs during isothermal ageing and not during quenching.

The radiation induced segregation model has been extended significantly in this work, but could also be developed to consider co-segregation of elements such as copper, molybdenum and manganese. This effect could only be considered in the radiation enhanced equilibrium segregation model, since the mechanism of radiation induced segregation by SIA-impurity complex migration cannot incorporate an additional element. The segregation behaviour of carbon requires more accurate quantification, which would require some detailed experimental work. However, this would in turn allow more accurate forecasting of the segregation of phosphorus.
The modelling of precipitation could also be further extended, possibly to predict the combined effects of irradiation-induced precipitation and segregation. This model may therefore be able to be used to give predictions for the ultra-fine copper precipitation that has been observed in many other RPV steels.

Finally, the Rate Theory modelling approach should be thoroughly investigated, owing to the recent work of English and Agnew that considers phosphorus segregation in bcc matrices. This would therefore enable a more direct comparison of predictions between the various modelling techniques, using the same irradiation conditions.
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Appendix A:

Program listings
Error Function Routine

This routine is used in most of the analytical segregation models. It requires an input number, and returns a value between 0 and 1.

erf:

If \( x > 3.554319 \) Then \( \text{erfx} = 1 \)

If \( x <= 1.5 \) Then
  \[
  \text{constant1} = \frac{2}{\sqrt{3.14159}} \\
  X1 = \left( x ^ 3 \right) / 3 \\
  X2 = \left( x ^ 5 \right) / 10 \\
  X3 = \left( x ^ 7 \right) / 42 \\
  X4 = \left( x ^ 9 \right) / 216 \\
  X5 = \left( x ^ {11} \right) / 1320 \\
  X6 = \left( x ^ {13} \right) / 5360 \\
  X7 = \left( x ^ {15} \right) / 75600 \\
  X8 = \left( x ^ {17} \right) / 685440 \\
  X9 = \left( x ^ {19} \right) / 6894720 \\
  \text{Sum} = x - X1 + X2 - X3 + X4 - X5 + X6 - X7 + X8 - X9 \\
  \text{erfx} = \text{constant1} \times \text{Sum}
  \]

End If

If \( x > 1.5 \) And \( x <= 3.554319 \) Then
  \[
  \text{constant1} = \frac{1}{\sqrt{3.14159}} \\
  \text{apprx} = \frac{\exp(-x ^ 2)}{x} \\
  \text{erfx} = 1 - \left( \text{constant1} \times \text{apprx} \right)
  \]

End If

If \( \text{erfx} > 1 \) Then \( \text{erfx} = 1 \)

Return
Binary ES model

This program includes subroutines to define the calculation parameters (subroutine checkval) and to output the results in a text format (subroutine save_results). These routines are used in subsequent programs in modified form to account for the different parameters that each program requires. Certain Visual Basic specific commands are also used, such as CommonDialog, which is one of a number of library functions.

GoSub checkval

i = 0
For T = (100 + 273.15) To (800 + 273.15) Step 10
i = i + 1
kT = k * T
Di = Dos * Exp(-Ea / kT)  'impurity element diffusion coefficient
max_ES = (B * Cg * Exp(Q / kT)) / (1 + (B * Cg * Exp(Q / kT)))
alpha_ES = max_ES / Cg
S = 2 * Sqr(Di * age_time) / (alpha_ES * gbw)
If S <= 3.5 Then
   GoSub erf
End If
C_ES = Cg + (max_ES - Cg) * (1 - Exp(s^2)) * (1 - erf)
Else
C_ES = max_ES
End If
C_ES • C_ES / Cg

Next T
GoSub save_results
Exit Sub

checkval:

k = 1.381E-23
Dos = Text1.Text
Ea = Text2.Text
B = Text3.Text
Cg = Text4.Text
Q = Text5.Text
gbw = Text6.Text
age_time = Text7.Text
Ea = Ea * 1.602E-19
Q = Q * 1.602E-19

Return

save_results:
'routine to output results to either text or comma delimited file

CommonDialog1.Flags = &H2
CommonDialog1.Filter = "All files (*.*)|*.|Text files(*.txt)|*.txt|Comma
delimited(*.csv)|*.csv|"'
CommonDialog1.filename = "results.txt"
CommonDialog1.FilterIndex = 2
CommonDialog1.Action = 2
filenum = FreeFile
If CommonDialog1.filename <> "" Then


Open CommonDialog1.filename For Output As filenum
Write #filenum, "Dos (m²/s)", Text1.Text
Write #filenum, "Sa (eV)", Text2.Text
Write #filenum, "B", Text3.Text
Write #filenum, "Cg (at%)", Text4.Text
Write #filenum, "Q (eV)", Text5.Text
Write #filenum, "gbw (m)", Text6.Text
Write #filenum, "ageing time (s)", Text7.Text
Write #filenum, "Equilibrium segregation during ageing model"
Write #filenum, "Temperature (°C)", "Segregation (Cb/Cg)", "Diffusion coefficient"

For i = 1 To 71
    Write #filenum, temp(i), conc(i), diff(i)
Next i
Close #filenum

End If
Return
End Sub
Effective time for linear cooling curves

This program determines effective cooling times assuming that the cooling rate is constant throughout. This program requires few parameters, so no separate routine is used. In addition, the subroutine to output the stored results is not given here.

If quench_number = 0 Then
    quench_number = quench_number + 1
    Ts = text1.Text + 273.15
    T0 = text2.Text + 273.15
    quench_time = text3.Text
    Ha = text4.Text * 1.6022-19
    cooltime = text5.Text
    k = 1.3815E-23
    highT = Ts
    Z = 0

For I = 1 To quench_time Step cooltime
    Z = Z + 1
    theta = (Ts - T0) / quench_time
    temp_diff = theta * cooltime
    lowT = highT - temp_diff
    eterm = Exp((-Ea * (Ts - lowT)) / (k * Ts * lowT))
    teffa = teffa + (cooltime * eterm)
    'store results in arrays
    t_quench(Z) = I
    upper_temp(Z) = highT - 273.15
    qr(Z) = theta
    'starting conditions for next cycle
    highT = lowT
    lowT = lowT - (theta * cooltime)
Next I

high_temp(1) = Ts - 273.15
low_temp(1) = T0 - 273.15
q_time(1) = quench_time
effect(1) = Format(teffa, "0.000")
effectT(1) = Format(teffa, "0.000")
new_effect(1) = Format(teffa, "0.000")

Else
    quench_number = quench_number + 1
    Do
        new_Ts = InputBox("Enter upper temperature", "Upper temperature")
        If new_Ts <> "" Then Exit Do
    Loop
    new_Ts = new_Ts + 273.15
    Do
        new_T0 = InputBox("Enter lower temperature", "Lower temperature")
        If new_T0 <> "" Then Exit Do
    Loop
    new_T0 = new_T0 + 273.15
    new_quench_time = InputBox("Enter quench time", "Quench time")
    If new_quench_time <> "" Then Exit Do
    Loop
    highT = new_Ts  'starting condition
    teffa = 0

For I = 1 To new_quench_time Step cooltime
    theta = (new_Ts - new_T0) / new_quench_time
    temp_diff = theta * cooltime
    lowT = highT - temp_diff
    eterm = Exp((-Ea * (new_Ts - lowT)) / (k * new_Ts * lowT))
    teffa = teffa + (cooltime * eterm)
    'store results in arrays
    t_quench(Z) = t_quench(Z - 1) + cooltime
    upper_temp(Z) = highT - 273.15
qr(z) = theta

'starting conditions for next cycle
highT = lowT
lowT = lowT - (theta * cooltime)
Z = Z + 1
Next I

teffb = (teffa * Exp((-Ea * (Ts - new Ts)) / (k * Ts * new Ts)))
teff = teff + teffb

high_temp(quench_number) = new Ts - 273.15
low_temp(quench_number) = new Ts - 273.15
effect(quench_number) = new quench_time
effectTs(quench_number) = Format(teffa, "0.000")
new_effect(quench_number) = Format(teff, "0.000")

End If

End Sub
Effective time for exponential cooling curves

This program determines effective cooling times assuming that the cooling rate is varying exponentially throughout. This program requires few parameters, so no separate routine is used. In addition, the subroutine to output the stored results is not given here.

If quench_number = 0 Then

quench_number = quench_number + 1

Ts = text1.Text + 273.15 'convert starting temperature from C to K
T0 = text2.Text + 273.15 'convert final temperature from C to K
quench_time = text3.Text 'total quench time (s)
Ea = text4.Text * 1.6022E-19 'convert from eV to J
cooltime = text5.Text 'increment for calculations of teff
k = 1.381E-23 'Boltzmann constant
Z = 0 'starting condition

For I = 1 To quench_time Step cooltime
  Z = Z + 1 'increment for calculations of teff
  theta = (Ts - T0) * (1 / ((quench_time * 2) / 10)) * Exp(-I / ((quench_time * 2) / 10))
  temp_diff = theta * cooltime 'temp change in cooltime secs of quench
  lowT = highT - temp_diff 'temp after cooltime seconds of quench
  eterm = Exp((-Ea * (Ts - lowT)) / (k * Ts * lowT))
  teff = teff + (cooltime * eterm)

'store results in arrays
  t_quench.Z = I
  upper_temp.Z = highT - 273.15
  qr.Z = theta

'starting conditions for next cycle
  highT = lowT
  lowT = lowT - (theta * cooltime)
Next I

high_temp(1) = Ts - 273.15
low_temp(1) = T0 - 273.15
q_time(1) = quench_time
effect(1) = Format(teff, "0.000")
effectTs(1) = Format(teff, "0.000")
new_effect(1) = Format(teff, "0.000")

Else

  quench_number = quench_number + 1

  Do
    new_Ts = InputBox("Enter upper temperature", "Upper temperature")
    If new_Ts <> "" Then Exit Do
  Loop
  new_Ts = new_Ts + 273.15

  Do
    new_T0 = InputBox("Enter lower temperature", "Lower temperature")
    If new_T0 <> "" Then Exit Do
  Loop
  new_T0 = new_T0 + 273.15

  Do
    new_quench_time = InputBox("Enter quench time", "Quench time")
    If new_quench_time <> "" Then Exit Do
  Loop
  highT = new_Ts 'starting condition
  teff = 0

  For I = 1 To new_quench_time Step cooltime
    theta = (new_Ts - new_T0) * (1 / ((new_quench_time * 2) / 10)) * Exp(-I / ((new_quench_time * 2) / 10))
    temp_diff = theta * cooltime 'temp change in cooltime secs of quench
    lowT = highT - temp_diff 'temp after cooltime seconds of quench
    eterm = Exp((-Ea * (new_Ts - lowT)) / (k * new_Ts * lowT))
  Next I
teffa = teffa + (cooltime * etern)

't store results in arrays
t_quench(Z) = t_quench(Z - 1) + cooltime
upper_temp(Z) = highT - 273.15
qr(Z) = theta

'starting conditions for next cycle
highT = lowT
lowT = lowT - (theta * cooltime)
Z = Z + 1
Next I

teffb = (teffa * Exp((-Ea * (Ts - new_Ts)) / (k * Ts * new_Ts)))
teff = teff + teffb

high_temp(quench_number) = new_Ts - 273.15
low_temp(quench_number) = new_T0 - 273.15
t_time(quench_number) = new_quench_time
effect(quench_number) = Format(teffa, "0.000")
effectTs(quench_number) = Format(teffb, "0.000")
new_effect(quench_number) = Format(teff, "0.000")

End If
End Sub
**TNES model**

This program determines the Thermal Non-Equilibrium Segregation concentration profile adjacent to the grain boundary. A number of parameters are required, which are defined in a separate subroutine.

'Model allows for possible desegregation if effective quench time is larger than the critical time for desegregation
'Model calculates area under enriched region of curve
'Curve calculated using equations from Hong Jiang
'Possible error in curve due to alpha equation incorporating Pi and a 4 instead of 2??

GoSub checkval
GoSub crit_time

'calculation for cbTNES
CbTNES = Cg * (EbTNES / EfV) * Exp(((EbTNES - EfV) / (k * Ts)) - ((EbTNES - EfV) / (k * Ta)))

GoSub quenchprofile
GoSub calc_integral
GoSub save_results

Exit Sub

checkval:

Emv = Text1.Text 'vacancy migration energy
EfV = Text2.Text 'vacancy formation energy
Cg = Text3.Text 'solute concentration
EbTNES = Text4.Text 'binding energy during TNES
Tmp = Text5.Text + 273.15 'convert Tmp from (C) to (K)
DcTNES = Text6.Text 'pre-exp for complex diffusion during TNES
EmCTNES = Text7.Text 'migration energy for diffn of complexes
d = Text8.Text 'grain size
DsTNES = Text9.Text 'pre-exp constant for solute diffusion
Es = Text10.Text 'activation energy for solute
Ts = Text12.Text + 273.15 'convert ST from (C) to (K)
teff = Text13.Text 'effective quench time from different program

'conversions
Es = Es * 1.602E-19 'convert Es from eV
Emv = Emv * 1.602E-19 'convert Emv from eV
EbTNES = EbTNES * 1.602E-19 'convert EbTNES from eV
EfV = EfV * 1.602E-19 'convert EfV from eV
EmCTNES = EmCTNES * 1.602E-19 'convert EmCTNES from eV

'temperatures
Ta = 0.5 * Tmp '-0.55Tmp
k = 1.381E-23 'Boltzmann's constant
delta = 0.05 'geometric constant
DcTNES = DcTNES * Exp(-EmCTNES / (k * Ta)) 'diffusivity of complexes
DsTNES = DsTNES * Exp(-Es / (k * Ts)) 'diffusivity of solute

Return

crit_time:
'calculation of critical time for desegregation

tcrit = (delta * (d ^ 2) * Log(DcTNES / DsTNES)) / (4 * (DcTNES - DsTNES))

Return
quenchprofile:
calculations from Hong's latest report
check each loop to compare effective quench time to critical time for desegregation
if \( t_{ef} - t_{crit} < 0 \) then perform calculations corresponding to desegregation regime

If \( t_{ef} - t_{crit} < 0 \) Then

\[
\text{results}(1, 0) = 0 \quad \text{distance from GB in 1st column of array}
\]
\[
\text{results}(2, 0) = \text{C发声NES} / \text{Cg} \quad \text{concentration in 2nd column of array}
\]

\[
w_d = 2 \times \text{we} \times (\text{C发声NES} - \text{Cg}) / \text{Cg}
\]

\[
\text{alpha} = \left(3.14159 \times \left(\text{C发声NES} ^ 2\right)\right) / \left(4 \times \text{D发声NES} \times t_{ef} \times \left(\text{Cg} ^ 2\right)\right)
\]

For \( i = 1 \) To 100000

\[
dist = i \times 0.000000001
\]

constant = \( \text{C发声NES} \times \exp(-\text{alpha} \times (\text{dist} ^ 2)) \)
If dist <= \( \text{we} \) Then \( \text{Cx} = \) constant
If dist <= \( (\text{we} + w_d) \) Then \( \text{Cx} = \left(\left((\text{dist} - \text{we}) / w_d\right) \times \text{Cg}\right) + \) constant
If dist > \( (\text{we} + w_d) \) Then \( \text{Cx} = \text{Cg} + \) constant

\[
\text{results}(1, i) = i
\]
\[
\text{results}(2, i) = \text{Cx} / \text{Cg}
\]
Next \( i \)

ElseIf \( t_{ef} >= t_{crit} \) Then

\[
\text{diff}_\text{coeff} = (\text{D发声NES} \times t_{crit}) / (\text{D发声NES} \times t_{ef})
\]
If \( \text{diff}_\text{coeff} > 1 \) Then \( \text{diff}_\text{coeff} = 1 \)

\[
\text{Cx_OTNES} = \left(\left(\text{C发声NES} - \text{Cg}\right) \times \text{Sqr}((\text{diff}_\text{coeff})) + \text{Cg}\right)
\]
\[
\text{results}(1, 0) = 0
\]
\[
\text{results}(2, 0) = \text{Cx_OTNES} / \text{Cg}
\]

If \( \text{diff}_\text{coeff} < 1 \) Then

\[
\text{we} = \left(\left(\text{Cg} / \text{Cx_OTNES}\right) \times 2 \times \text{Sqr}((\text{D发声NES} \times (t_{ef} - t_{crit}))\right) \quad \text{use solute diff coeff}
\]
Else

\[
\text{we} = \left(\left(\text{Cg} / \text{Cx_OTNES}\right) \times 2 \times \text{Sqr}((\text{D发声NES} \times (t_{ef} - t_{crit})))\right) \quad \text{use complex diff coeff}
\]
End If

\[
w_d = 2 \times \text{we} \times (\text{Cx_OTNES} - \text{Cg}) / \text{Cg}
\]

If \( \text{diff}_\text{coeff} < 1 \) Then

\[
\text{alpha} = \left(\left(\text{Cx_OTNES} ^ 2\right)\right) / \left(4 \times \text{D发声NES} \times (t_{ef} - t_{crit}) \times \left(\text{Cg} ^ 2\right)\right)
\]
\[
\text{alpha} = \left(3.14159 \times \left(\text{Cx_OTNES} ^ 2\right)\right) / \left(4 \times \text{D发声NES} \times (t_{ef} - t_{crit}) \times \left(\text{Cg} ^ 2\right)\right)
\]
\[
\text{alpha} = \left(\left(\text{Cx_OTNES} ^ 2\right)\right) / \left(4 \times \text{D发声NES} \times (t_{ef} - t_{crit}) \times \left(\text{Cg} ^ 2\right)\right)
\]
\[
\text{alpha} = \left(3.14159 \times \left(\text{Cx_OTNES} ^ 2\right)\right) / \left(4 \times \text{D发声NES} \times (t_{ef} - t_{crit}) \times \left(\text{Cg} ^ 2\right)\right)
\]
End If

For \( i = 1 \) To 100000

\[
dist = i \times 0.000000001
\]

constant = \( \text{C发声NES} \times \exp(-\text{alpha} \times (\text{dist} ^ 2)) \)
If dist <= \( \text{we} \) Then \( \text{Cx} = \) constant
If we <= \( \text{dist} <= (\text{we} + w_d) \) Then \( \text{Cx} = \left(\left((\text{dist} - \text{we}) / w_d\right) \times \text{Cg}\right) + \) constant
If dist > \( (\text{we} + w_d) \) Then \( \text{Cx} = \text{Cg} + \) constant

\[
\text{results}(1, i) = i
\]
\[
\text{results}(2, i) = \text{Cx} / \text{Cg}
\]
Next \( i \)
'calculations for teff
results(3, 0) = CbTNES / Cg  'concentration in 2nd column of array

we = (Cg / CbTNES) * Sqr(2 * DcTNES * tcrit)
wd = 2 * we * (CbTNES - Cg) / Cg

alpha = (3.14159 * (CbTNES ^ 2)) / (4 * DcTNES * tcrit * (Cg ^ 2))

For i = 1 To 1000000
  dist = i * 0.0000000001
  constant = CbTNES * Exp(-alpha * (dist ^ 2))
  If dist <= we Then Cx = constant
  If we < dist <= (we + wd) Then Cx = ((dist - we) / wd) * Cg + constant
  If dist > (we + wd) Then Cx = Cg + constant
  results(3, i) = Cx / Cg
Next i
End If

Return

calc_integral:
'subroutine to calculate the area under the curve within the enriched region
'the routine loops until the value of Cx/Cg stored in the results array becomes <= 1
'the routine stores the sum of the concentration as variable INTEGRAL
'the routine stores the width of enrichment as W_ENRICH

integral = 0
i = 0

Do
  w_enrich = i
  If i = 1001 Then Exit Do
  If results(2, i) <= 5 Then Exit Do
  integral = integral + (results(2, i) - 5)
  i = i + 1
Loop

w_enrich = w_enrich - 1  'since loop adds 1 until the value is less than 5

Return
End Sub
**Ternary RIS model**

The program presented returns predictions for both binary and ternary Radiation Induced Segregation. Calculations are also performed for radiation enhanced equilibrium segregation during service life.

GoSub check_val

'3 sections to program
' calculate Fe-P predictions incorporating irradiation enhanced diffusion
' calculate Fe-C predictions
' calculate Fe-C-P predictions

GoSub binary_a
GoSub binary_b
GoSub ternary

GoSub save_results

Exit Sub

check_val:
  k = 1.381E-23  'Boltzmanns constant
  delta = 0.05  'delta, numerical constant
  A = 1  'constant: vibrational entropy of atoms around point defect
  av = 1  'constant: vibrational entropy of atoms around vacancy

P0 = Text1.Text  'P0=dislo density parameter (m^-2)
R = Text2.Text  'R=grain size (um)
R = R * 0.000001  'convert R from um to m
G = Text3.Text  'G=dpa/s
dose = Text4.Text  'dose=dose (dpa)
drcf = Text5.Text  'drcf=dose rate correction factor
Gc = G * drcf  'corrected dose rate
Zl = Text6.Text  'interstitial bias
gbw = Text7.Text  'grain boundary width

Emi = Text8.Text  'mig energy for diff of interstitials (eV)
Doi = Text9.Text  'pre-exp const for diff of interstitials (m2/s)
Env = Text10.Text  'migration energy for vacancy diffusion (eV)
Dov = Text11.Text  'pre-exp const for vacancy diffusion (m2/s)
EfV = Text12.Text  'vacancy formation energy (eV)
Efi = Text13.Text  'interstitial formation energy (eV)
Ed = Text14.Text  'activation energy for dislocation recovery (eV)
Fl = Text15.Text  'jump distance of interstitials (m)
B = Text16.Text  'B-equilibrium segregation parameter

Eia = Text17.Text  'activation energy for solute diff (eV)
Dosa = Text18.Text  'pre-exp const for solute diff (m2/s)
Cga = Text19.Text  'solute conc in matrix (at fr)
Ebia = Text20.Text  'solute interstitial (S-I) binding energy (eV)
EmCa = Text21.Text  'migration energy for diffusion of S-I complexes (eV)
DoCa = Text22.Text  'pre-exp constant for diff of S-I complexes (m2 s^-1)
Qa = Text23.Text  'equilibrium segregation energy

Eib = Text24.Text  'activation energy for solute diff (eV)
Dobs = Text25.Text  'pre-exp const for solute diff (m2/s)
Cgb = Text26.Text  'solute conc in matrix (at fr)
Ehb = Text27.Text  'solute interstitial (S-I) binding energy (eV)
EmCb = Text28.Text  'migration energy for diffusion of S-I complexes (eV)
DcCb = Text29.Text  'pre-exp constant for diff of S-I complexes (m2 s^-1)
Qb = Text30.Text  'equilibrium segregation energy

Eni = Eml * 1.602E-19
ENV = Enm * 1.602E-19
EFv = EfV * 1.602E-19
Ef1 = Efi * 1.602E-19
ED = Ed * 1.602E-19
Eia = Eia * 1.602E-19
Ebia = Ebia * 1.602E-19
Eba = Abs(Ebia)
EmCa = EmCa * 1.602E-19
Qa = Qa * 1.602E-19
Ebib = Ebib * 1.602E-19
EmCb = EmCb * 1.602E-19
Qb = Qb * 1.602E-19

Return

binary_a;
If Cga > 0 Then
  i = 0
  For Ti = (100 + 273.15) To (610 + 273.15) Step 10
    kT = (k * Ti)
    i = i + 1
    'segregation during irradiation
    P = P0 * Exp(Rd / kT)  'dislocation recovery
    kdi2 = Zi * P + (6 / R) * Sqr(Zi * P)  'interstitial sink strength
    kdv2 = P + (6 / R) * Sqr(P)  'vacancy sink strength
    Dv = Dov * Exp(-Emv / kT)  'vacancy diffusion coefficient
    Dia = Dosa * Exp(-Eia / kT)  'element a diffusion coefficient
    Di = Dosi * Exp(-Emi / kT)  'interstitial diffusion coefficient
    Dca = DoCa * Exp(-EmCa / kT)  'S-I complex diffusion coefficient
    lambda = 21 * Di / (Fi * 2)  'lambda, the long range recombination
    eta = 4 * lambda * Gc / (kdi2 * kdv2 * Dv * Di)  'eta, equation 7 in paper
    Feta = (2 / eta) * (Sqr(l + eta) - 1)  'F(eta), equation 6 in paper
    'irradiation enhanced diffusion
    Cve = av * Exp(-Rfv / kT)  'thermal equilibrium vacancy conc
    Cvr = Gc * Feta / (Dv * kdv2)  'conc of irrad created point defects
    Y = (Cve + Cvr) / Cve  'irradiation enhancement ratio
    If Check1.Value = 1 Then
      Dia = Dia * Y  'irrad enhanced solute diff coefficient
      End If
    'max RIS P, C_maxRIS_a
    'use absolute value of Ebia, Eba
    If Check3.Value = 1 Then
      C_maxRIS_a = Cga + (Cga * Eba / Efi) * (1 + (Gc * Feta / (A * Di + kdi2)) * Exp(Efi / kT))
    Else
      C_maxRIS_a = Cga + (Cga * (1 + (Gc * Feta / (A * Di + kdi2)) * Exp(Efi / kT))
    End If
    'segregation during irradiation
    alpha_RIS_a = C_maxRIS_a / Cga  'alpha_RIS_a=enrichment for element a
    'calculation of saturation time, tcrit_a, for (element a)
    tcrit_a = delta * R^2 * Log(Dca / Dia) / (4 * (Dca - Dia))
    t = dose / G  'compare irradiation time, t, with saturation time for element a, tcrit_a
    If t > tcrit_a Then
      t = tcrit_a
      S = 2 * Sqr(Dca * t) / (alpha_RIS_a * gbw)
      If S <= 3.5 Then
        GoSub erf
        C_RIS_a = Cga + (C_maxRIS_a - Cga) * (1 - Exp(S^2) * (1 - erf(S))
      Else
        C_RIS_a = C_maxRIS_a
      End If
    End If
Else
    \( S = 2 \times \text{Sqr}(DCa \times t) / (\alpha_{\text{RIS}_a} \times \text{gbw}) \)
    If \( S \leq 3.5 \) Then
        GoSub erfx
        \( C_{\text{RIS}_a} = C_ga + (C_{\text{maxRIS}_a} - C_ga) \times (1 - \text{Exp}(S^2) \times (1 - \text{erfx})) \)
    Else
        \( C_{\text{RIS}_a} = C_{\text{maxRIS}_a} \)
    End If
End If

'\( \text{RIS} \) enrichment ratio
\( C_{\text{RIS}_a} = C_{\text{RIS}_a} / C_ga \)

'check for -ve binding energy
If \( C_{\text{RIS}_a} \geq 1 \text{ And } E_{\text{bia}} < 0 \) Then
    \( C_{\text{RIS}_a} = 1 / C_{\text{RIS}_a} \)
End If

'equilibrium segregation
'max ES (element a)
\( C_{\text{maxES}_a} = (B \times C_ga \times \text{Exp}(Q_a / kT)) / (1 + (B \times C_ga \times \text{Exp}(Q_a / kT))) \)

'ES enrichment ratio for element a
\( \alpha_{\text{ES}_a} = C_{\text{maxES}_a} / C_{\text{ES}_a} \)
\( t = \text{dose} / G \)
\( S = 2 \times \text{Sqr}(Dia \times t) / (\alpha_{\text{ES}_a} \times \text{gbw}) \)
If \( S \leq 3.5 \) Then
    GoSub erfx
    \( C_{\text{ES}_a} = C_ga + (C_{\text{maxES}_a} - C_ga) \times (1 - \text{Exp}(S^2) \times (1 - \text{erfx})) \)
Else
    \( C_{\text{ES}_a} = C_{\text{maxES}_a} \)
End If

'\( \text{ES} \) enrichment ratio
\( C_{\text{ES}_a} = C_{\text{ES}_a} / C_ga \)

'combined enrichment ratio
\( C_{\text{comb}_a} = C_{\text{RIS}_a} + C_{\text{ES}_a} - 1 \)

'convert temp to C from K
\( \text{Temp} = \text{Ti} - 273.15 \)

fe_p1(i) = Temp
fe_p2(i) = C_{\text{RIS}_a}
fe_p3(i) = C_{\text{ES}_a}
f4_p4(i) = C_{\text{comb}_a}

Next Ti
Else
    MsgBox "No (element a)!"
End If
Return

binary_b:
If Cgb > 0 Then
    \( i = 0 \)
For Ti = (100 + 273.15) To (610 + 273.15) Step 10
    \( kT = (k \times \text{Ti}) \)
    \( i = i + 1 \)
    'segregation during irradiation
    \( P = P_0 \times \text{Exp}(ED / kT) \)
    \( kdi2 = Z_i + P + (6 / R) \times \text{Sqr}(Z_i \times P) \)
    \( kdv2 = P + (6 / R) \times \text{Sqr}(P) \)
    \( D_v = D_{ov} \times \text{Exp}(-Emv / kT) \)
    \( D_{ib} = D_{oib} \times \text{Exp}(-Eib / kT) \)
    \( D_i = D_{oi} \times \text{Exp}(-Emi / kT) \)
    \( D_{cb} = D_{ocb} \times \text{Exp}(-Emcb / kT) \)
    'dislocation recovery
    'interstitial sink strength
    'vacancy sink strength
    'vacancy diffusion coefficient
    'solute (carbon) diffusion coefficient
    'interstitial diffusion coefficient
    'S-I complex diffusion coefficient
\[ \lambda = 21 \times \frac{D_i}{(F_i \times 2)} \]

\[ \eta'' = 4 \times \lambda \times \frac{G_c}{(D_{v} \times k_{d12} \times k_{d2} \times D_i)} \]

\[ \eta''' = \frac{2}{\eta} \times \left( \sqrt{\lambda + \eta'} - 1 \right) \]

\[ Y = \frac{C_{v} + C_{r}}{C_{v}} \]

If Check2.Value = 1 Then

\[ D_i = D_i \times Y \]

End If

'irradiation enhanced solute diff coeff

'segregation during irradiation

\[ \alpha_{RIS_b} = C_{maxRIS_b} / C_{gb} \]

'check for -ve binding energy

If \( C_{RIS_b} \) >= 1 And \( E_{b} \) < 0 Then

\[ C_{RIS_b} = \frac{1}{C_{RIS_b}} \]

End If

'equilibrium segregation

\[ C_{ES_b} = \frac{(8 \times C_{gb} \times \exp(Q_b / KT))}{(1 + (8 \times C_{gb} \times \exp(Q_b / KT)))} \]

\[ \alpha_{ES_b} = \frac{C_{maxES_b}}{C_{gb}} \]

\[ t = \frac{\text{dose}}{G} \]

\[ S = 2 \times \sqrt{D_i \times t} \]

If \( S \leq 3.5 \) Then

\[ C_{ES_b} = C_{gb} + (C_{maxES_b} - C_{gb}) \times (1 - \exp(S^2) \times (1 - \text{erf}(S))) \]

Else

\[ C_{ES_b} = C_{maxES_b} \]

End If

'Smax ES (element b)

\[ C_{maxES_b} = \frac{(8 \times C_{gb} \times \exp(Q_b / KT))}{(1 + (8 \times C_{gb} \times \exp(Q_b / KT)))} \]

'ES enrichment ratio

\[ \alpha_{ES_b} = \frac{C_{maxES_b}}{C_{gb}} \]

\[ t = \frac{\text{dose}}{G} \]

\[ S = 2 \times \sqrt{D_i \times t} \]

If \( S \leq 3.5 \) Then

\[ C_{ES_b} = C_{gb} + (C_{maxES_b} - C_{gb}) \times (1 - \exp(S^2) \times (1 - \text{erf}(S))) \]

Else

\[ C_{ES_b} = C_{maxES_b} \]

End If
C_ES_b = C_maxES_b
End If

'ES enrichment ratio
C_ES_b = C_ES_b / Cgb

C_comb_b = C_RIS_b + C_ES_b - 1 'combined enrichment ratio

'convert temp from K to C
Temp = Ti - 273.15
fe_c1(i) = Temp
fe_c2(i) = C_RIS_b
fe_c3(i) = C_ES_b
fe_c4(i) = C_comb_b

Next Ti
Else
MsgBox "No (element b)!
End If
Return

ternary:
'ternary calculations for (element a) and (element b)
'RIS and ES
'irradiation enhanced diffusion for (element a) only!
If Cga > 0 And Cgb > 0 Then
i = 0
For Ti = (100 + 273.15) To (610 + 273.15) Step 10
kT = (k * Ti)
i = i + 1
'RIS
P = P0 * Exp(kd / kT)
kd2 = Z1 * P + (6 / R) * Sqr(Z1 * P)
kd2 = P + (6 / R) * Sqr(P)
Dv = Dov * Exp(-Ev / kT)
Dia = Doa * Exp(-Eia / kT)
Dib = Dobs * Exp(-Eib / kT)
Di = Dio * Exp(-Eio / kT)
DCa = DoCa * Exp(-Eca / kT)
DCB = DoCB * Exp(-Ecb / kT)
lambda = Z1 * Di / (Pi * 2)
etta = 4 * lambda * Gc / (kd2 * kdv2 * Dv * Di) 'eta, equation 7 in paper
Feta = (2 / eta) * (Sqr(1 + eta) - 1) 'F(eta), equation 6 in paper

'irradiation enhanced diffusion
Cve = av * Exp(-Ev / kT)
Cvr = Gc * Feta / (Dv * kdv2)
Y = (Cve + Cvr) / Cve 'irradiation enhancement ratio

If Check1.Value = 1 Then
Dia = Dia * Y
End If

If Check2.Value = 1 Then
Dib = Dib * Y
End If

If Check3.Value = 1 Then
C_maxRIS_a = Cga + (Cga * Eba / Efi) * ((Cga * Exp(Eba / kT)) / (Cga * Exp(Eba / kT)) + (Cgb * Exp(Ebb / kT))) * (1 + Gc * Feta / (A * Di * kd2))
Else
C_maxRIS_a = Cga
End If
\[ C_{\text{maxRIS}_a} = C_{ga} + \left( C_{ga} \cdot \left( \frac{\exp\left( \frac{E_{ba}}{kT} \right)}{\exp\left( \frac{E_{ba}}{kT} \right) + \left( \frac{C_{gb}}{1 + \frac{(G_c \cdot F_{eta})}{(A \cdot D_i \cdot k_{di2})} \cdot \exp\left( \frac{E_{fi}}{kT} \right)} \right)} \right) \right) \]

If Check4.Value = 1 Then
\[ C_{\text{maxRIS}_b} = C_{gb} + \left( C_{gb} \cdot \left( \frac{\exp\left( \frac{E_{bb}}{kT} \right)}{\exp\left( \frac{E_{bb}}{kT} \right) + \left( \frac{C_{gb}}{1 + \frac{(G_c \cdot F_{eta})}{(A \cdot D_i \cdot k_{di2})} \cdot \exp\left( \frac{E_{fi}}{kT} \right)} \right)} \right) \right) \]
End If

End If

segregation level during irradiation
alpha_{RIS}_a = \frac{C_{\text{maxRIS}_a}}{C_{ga}} \quad \text{alpha}_{RIS}_a=RIS\text{ enrichment for element } a
\]

alpha_{RIS}_b = \frac{C_{\text{maxRIS}_b}}{C_{gb}} \quad \text{alpha}_{RIS}_b=RIS\text{ enrichment for element } b

'calculation of saturation time, tcrit_a, for element a
\[ tcrit_a = \delta \cdot R^2 \cdot \log\left( \frac{D_{Ca}}{D_{ia}} / \left( 4 \cdot (D_{Ca} - D_{ia}) \right) \right) \]

\[ t = \text{dose} / G \]

'threshold irradiation time, t, with saturation time, tcrit_a
If t > tcrit_a Then
\[ S = 2 \cdot \sqrt{D_{Ca} \cdot t} / (\alpha_{RIS}_a \cdot \text{gbw}) \]
End If

'compare irradiation time t with saturation time, tcrit_b
If t > tcrit_b Then
\[ S = 2 \cdot \sqrt{D_{Cb} \cdot t} / (\alpha_{RIS}_b \cdot \text{gbw}) \]
End If

'corrected conc allowing for site competition at GB
'predicted concentration used (C_{RIS}_b)
\[ C_{RIS}_a = C_{RIS}_a \cdot \left( \frac{C_{RIS}_a \cdot \exp\left( \frac{Q_a}{kT} \right)}{\exp\left( \frac{Q_a}{kT} \right) + \left( \frac{e_{RIS_a \cdot E_{pia}}}{-kT} \right)} \right) \]
\[ C_{RIS}_a = C_{RIS}_a / C_{ga} \]
C_RIS_b = C_RIS_b * (C_RIS_b * Exp(Qb / kT) / ((C_RIS_b * Exp(Qa / kT)) + (C_RIS_b * Exp(Qb / kT))))

C_RIS_b = C_RIS_b / C_gb

'check for -ve binding energy
If C_RIS_a > 1 And Ebia < 0 Then
  C_RIS_a = 1 / C_RIS_a
End If

'check for -ve binding energy
If C_RIS_b > 1 And Ebib < 0 Then
  C_RIS_b = 1 / C_RIS_b
End If

'EQUILIBRIUM SEGREGATION

'maximum equilibrium segregation, C_maxES_a
C_maxES_a = (Cga * Exp(Qa / kT)) / (1 + (Cga * Exp(Qa / kT)) + (Cgb * Exp(Qb / kT)))

'maximum equilibrium segregation, C_maxES_b for carbon equation 26b in paper
C_maxES_b = (Cgb * Exp(Qb / kT)) / (1 + (Cga * Exp(Qa / kT)) + (Cgb * Exp(Qb / kT)))

'alpa_ES_a=ES enrichment ratio for element a
alpha_ES_a = C_maxES_a / Cga

'alpa_ES_b=ES enrichment ratio for element b
alpha_ES_b = C_maxES_b / C_gb

t = dose / G

'equilibrium segregation calculations for element a
S = 2 * Sqr(Dia * t) / (alpha_ES_a * gbw)
If S <= 3.5 Then
  GoSub erfx
  C_ES_a = Cga + (C_maxES_a - Cga) * (1 - Exp(S^2)) * (1 - erfx))
Else
  C_ES_a = C_maxES_a
End If

'alpa_ES_enrichment ratio for element a
C_ES_a = C_ES_a / Cga

'alpa_ES_enrichment ratio for element b
S = 2 * Sqr(Dib * t) / (alpha_ES_b * gbw)
If S <= 3.5 Then
  GoSub erfx
  C_ES_b = Cgb + (C_maxES_b - Cgb) * (1 - Exp(S^2)) * (1 - erfx))
Else
  C_ES_b = C_maxES_b
End If

'alpa_ES_enrichment ratio for element b
C_ES_b = C_ES_b / C_gb

C_comb_a = C_RIS_a + C_ES_a 'add RIS to equilibrium for element a
C_comb_b = C_RIS_b + C_ES_b 'add RIS to equilibrium for element b
Temp = Ti - 273.15 'convert temp to degC

'write results to arrays
results1(i) = Temp 'temp
results2(i) = C_RIS_a 'RIS of element a
results3(i) = C_RIS_b 'RIS of element b
results4(i) = C_ES_a 'equilibrium seg of element a
results5(i) = C_ES_b 'equilibrium seg of element b
results6(i) = C_comb_a 'combined element a
results7(i) = C_comb_b 'combined element b

Next Ti
Else
  MsgBox "Unable to perform ternary predictions"
End If
Return
End Sub
Precipitation model

GoSub checkval  'set up variables
GoSub quenchprofile  'to establish TNES profile after quench using tEH

' to establish TNES profile during ageing
If (Ta - Tmp) > 0 Then GoSub TaGTmp Else GoSub TaLTmp

GoSub save_results  'output results to .txt file
Exit Sub

checkval:
Ts = Text1.Text  'Starting temp for quench (K)
teff = Text2.Text  'effective quench time (s)
Tm = Text3.Text  'ageing temperature (K)
deltat = Text4.Text  'ageing time (hrs)
Twp = Text5.Text  'melting temp of material (K)
Eb = Text6.Text  'binding energy (eV/atom)
Efv = Text7.Text  'vacancy formation energy (eV/atom)
Ea = Text8.Text  'activation energy (eV/atom)

tse = Text9.Text  'solute concentration (at%)
vse = Text10.Text  'carbon concentration (wt%)
d = Text11.Text  'grain size (m)
gbw = Text12.Text  'grain boundary width (m)
a = Text13.Text  'lattice parameter (m)
chi = Text14.Text  'angle between ppt and GB (°)

Qv = Text15.Text  'pre-exp for solute (vol) diff (m²/s)

ab = Text16.Text  'pre-exp for solute (GB) diff (m²/s)

Qb = Text17.Text  'activation energy for solute (GB) diffusion (J/mol)

DvS = Text18.Text  'activation energy for solute (volume) diffusion (J/mol)

DoC = Text19.Text  'pre-exp for complex diff (m²/s)

roalpha = Text20.Text  'molar density of matrix (mol/m³)

vtheta = Text21.Text  'molar density of ppt phase (mol/m³)

xtheta = Text22.Text  'at.fr. of solute in nucleus (mol.fr.)

sigmaab = Text23.Text  'matrix/ppt interfacial energy (J/m²)

DbsTs = Text24.Text  'matrix/ppt facet int. energy (J/m²)

k = 1.381E-23  'Boltzmanns constant (J/K)
NA = 6.022E+23  'Avagadros number (atoms/mol)

R = 8.314  'Gas constant used with deltaH (J/K mol)

Ccc = Cu * 0.03573  'convert from wt.% to at.%

chi = chi * (3.1415927 / 180)

tage = tage * 3600  'converts ageing time from hours to seconds
deltat = deltat * 3600  'converts time interval from hours to seconds

'through from Senior report, Nuclear Electric

Cc = Cu * 0.03573  'convert from wt.% to at.%

Chi = Chi * (3.1415927 / 180)

'through from Senior report, Nuclear Electric

DvS = av * Exp(-Qv / (R * Ts))  '@ Ts for segregation model
DvSTa = av * Exp(-Qv / (R * Ta))  '@ Ta for pptn model

'DbsTs = ab * Exp(-Qb / (R * Ts))  '@ Ts for GB diffusion model
DbsTs = ab * Exp(-Qb / (R * Ta))  '@ Ta for GB diffusion model

'DcTs = DoC * Exp(-Ea / (k * Ts))  'diff coeff @ Ts, DcTs
\[ DcTa = DoC \cdot \exp\left(-\frac{Ea}{(k \cdot Ta)}\right) \quad \text{'diff coeff @ Ta, DcTa} \]

\[ \text{'critical time @ Ta, } tcTa \text{ (seconds)} \]
\[ tcTa = (\deltaa \cdot (d^2) \cdot \log(DcTa / DvsTa)) / (4 \cdot (DcTa - DvsTa)) \]

\[ \text{'critical time @ Ta, } tcTa \text{ (seconds)} \]
\[ tcTa = (\deltaa \cdot (d^2) \cdot \log(DcTa / DvsTa)) / (4 \cdot (DcTa - DvsTa)) \]

\[ \text{'tcc (seconds) used in calculations for coarsening} \]
\[ tcc = \frac{(\deltaa \cdot (d^2) \cdot \log(DcTs / OvsTs)}{(4 \cdot (DCTS - OvsTs)} \]

\[ \text{'critical time @ Ta, } tcTa \text{ (seconds)} \]
\[ tcTa = (\deltaa \cdot (d^2) \cdot \log(DcTa / DvsTa)) / (4 \cdot (OcTa - DvsTa)} \]

\[ \text{'boundary concentration} \]
\[ Cb = Cg \cdot \left(\frac{E_b}{E_{fv}}\right) \cdot \exp\left(-\frac{(E_b - E_{fv})}{(k \cdot Tmp)}\right) \]

Return

quenchprofile:

'determine initial profile and stores in arrays distance and quench
'distance contains the distance from GB
'quench contains the concentration ratio figures
'routine splits the profile into 3 regions: enriched (x<we), depleted (we<x<we+wd) and the rest (x>we+wd)

\[ CbQ = Cb \]
\[ we = (Cg / CbQ) \cdot \sqrt{2 \cdot DcTs} \cdot \text{teff} \]
\[ wd = 2 \cdot we \cdot (CbQ - Cg) / Cg \]
\[ \alpha = (3.14159 \cdot (CbQ^2)) / (8 \cdot DcTs \cdot \text{teff} \cdot (Cg^2)) \]

\[ \text{distance}(0) = 0 \]
\[ \text{quench}(0) = CbQ / Cg \]
\[ xb = 0 \]

For i = 1 To 10000 Step 1
\[ \text{dist} = i \cdot 0.000000001 \]
\[ \text{constant} = CbQ \cdot \exp(-\alpha \cdot (\text{dist}^2)) \]
If dist <= we Then
\[ \text{Cx} = \text{constant} \]
ElseIf we < dist <= (we + wd) Then
\[ \text{Cx} = ((\text{dist} - we) / wd) \cdot Cg + \text{constant} \]
ElseIf dist > (we + wd) Then
\[ \text{Cx} = Cg + \text{constant} \]
End If
\[ \text{distance}(i) = \text{dist} \]
\[ \text{quench}(i) = \text{Cx} / Cg \]
Next i

Return

TaLTmp:

'ageing temperature is less than Tmp
'diffusion coefficient is recalculated for the ageing temperature
'store segregation profile in array results3

\[ CbA = Cb \]
\[ \text{results3}(0) = CbA / Cg \]
\[ we = (Cg \cdot \sqrt{2 \cdot DcTs} \cdot \text{teff}) / CbA \ 'these values still use diff coeff \]
\[ \text{corresponding to } Tmp, \text{is after quench} \]
\[ \text{wd} = (2 \cdot we \cdot (CbA - Cg)) / Cg \]
\[ \alpha = (3.14159 \cdot (CbA^2)) / (8 \cdot DcTs \cdot \text{teff} \cdot (Cg^2)) \]

GoSub nucleation \quad 'determines collector plate areas prior to growth

\[ z = 0 \]
\[ g = 0 \]

For t = deltat To tage Step deltat \quad 'step through loop until total ageing time is reached
\[ 'time is in seconds, increment is deltat, which is usually 3 seconds \]
\[ 'for t<tcc then the growth calculations are made \]

\[ L = 0 \]
\[ G = 0 \]

For i = 1 To 10000 Step 1
\[ \text{dist} = i \cdot 0.000000001 \]
\[ \text{constant} = CbA \cdot \exp(-\alpha \cdot (\text{dist}^2)) \]
If dist <= we Then
\[ \text{Cx} = \text{constant} \]
ElseIf we < dist <= (we + wd) Then
\[ \text{Cx} = ((\text{dist} - we) / wd) \cdot Cg + \text{constant} \]
ElseIf dist > (we + wd) Then
\[ \text{Cx} = Cg + \text{constant} \]
End If
\[ \text{distance}(i) = \text{dist} \]
\[ \text{quench}(i) = \text{Cx} / Cg \]
Next i

Return
'for t>tcc then the coarsening calculations are made

\[ z = z + 1 \]

\( z \) is used to determine number of cycles performed

\[ \text{cnst} = 2 \times \text{Sqr}(\text{DcTa} \times t) \]

This loop calculates conc ratios for up to 500nm from the GB

'concc profile is stored in results3 and is overwritten each loop

For cont = 1 To 10000

\[ \text{dist} = \text{cont} \times 0.00000001 \]

constant = CB * Exp(-alpha * dist ^ 2)

If dist => we Then

\[ x = (\text{dist} - \text{we}) / \text{cnst} \]

GoSub erf

Cxi = Cg + erf * ((dist - we) * Cg) / wd

C2 = Exp((-dist - we ^ 2) / (cnst ^ 2)) * ((Cg * cnst) / (wd * Sqr(3.14159)))

\[ x = (\text{wd} + \text{dist} - \text{we}) / \text{cnst} \]

GoSub erf

erfxi = erf

\[ x = (\text{wd} - \text{dist} + \text{we}) / \text{cnst} \]

GoSub erf

Cx3 = (-Cg / 2) * (erfx + erfx1)

Cx4 = ((-Cg * Sqr(DcTa * t)) / (wd * Sqr(3.14159))) * (Exp((-wd + dist - we) ^ 2) / (cnst ^ 2)) + Exp((-wd - dist + we) ^ 2) / (cnst ^ 2))

Cx5 = (-(dist * Cg) / (2 * wd)) * (erfx1 - erf)

'could be dist-we

\[ x = \text{constant} + Cxi + Cx2 + Cx3 + Cx4 + Cx5 \]

ElseIf dist < we Then

\[ x = \text{constant} \]

End If

results3(cont) = Cx / Cg

Next cont

If t - tcc < 0 Then

GoSub growth

Else

GoSub coarsening

End If

Next t

Return

nucleation:

'predictions of precipitate nucleation time and size during ageing

'equations from Hong's paper

'set xb equal to Cb

\[ \text{xb} = \text{Cb} \]

'c = \log((\text{Cg} * (\text{Cc} ^ \text{Xe})) + (\text{deltaH2} / (\text{R2} * \text{Tsolv})))

'This equation from Hong's last report

\( c = -0.9 \)

'\( c = -0.9 \) taken from Carolan table 8

'Gibbs-Thompson effect??

'see carolan paper equation 2a

\( \exp((2 * \text{sigmabc} + \text{omeg}) / (\text{R} * \text{Tage} * \text{rprime})) \)

\[ \text{xTage} = ((1 / \text{Cc}) \times \exp((-\text{deltaH} / (\text{R} * \text{Ta}) + c)) ^ (6 / 23)) \]

\[ \text{cap_base} = (2 / \sin(\text{chi})) \times ((1 / \sin(\text{chi})) - (1 / \tan(\text{chi}))) \]

\[ \text{sigma} = (\text{sigmabc} - \text{cap_base}) + \text{sigmabc} - \text{sigmabb} \]

'driving force for the formation of a particle

'equation 12 from Hong's paper

\[ \text{delG} = ((\text{R} * \text{Ta}) / (2 * \text{Vtheta})) \times \log(\text{xb} / \text{xTage}) \]

'Gibbs free energy of critical GB precipitate nucleus formation

\[ \text{dstar} = ((4 * 3.14159 * (\text{sigma} ^ 3)) / (3 * (\text{delG} ^ 2))) \times (2 - (3 * \cos(\text{chi}) + (\cos(\text{chi}) ^ 3))) \]

'critical nucleus size

'equation A5 from Carolan

\( \text{L0} = (2 \times \text{sigma}) / \text{delG} \)
total number of atoms per unit area of GB
\[ N = gw \cdot ralpha \cdot NA \]

number of critical precipitate nuclei per unit area of GB
\[ N_n(O) = (N / xtheta) \cdot \exp(-dG^*/(k \cdot Ta)) \]

no of ppt's stored in array \( N_n \)

mean area of the collector plate area
\[ A_m(O) = 1 / N_n(O) \]

incubation time of the nucleation at temperature \( Ta \), \( \tau \)
\[ \tau = (32 \cdot k \cdot Ta \cdot (a^4) \cdot (\sigma^2) \cdot (NA^2)) / (D_{bTa} \cdot gw \cdot xB \cdot (V_{theta}^2) \cdot (deltaGv^3) \cdot \sin(chi)) \]

min area of collector plate

\[ A_{min} = 2E-18 \]

\[ A_{min} = 16 \cdot obsTa \cdot \tau \]

sdev = \( (Am(O) - A_{min}) / 3 \) 'standard deviation

\[ sdev = \text{Abs}(sdev) \]

\[ \text{ppt\_size}(0) = 10 \]

determine volume of one ppt
\[ \text{ppt\_volume}(0) = ((2 / 3) \cdot 3.14159 \cdot (\text{ppt\_size}(0) / \sin(chi)) \cdot 3) \cdot (1 - \cos(chi)) \]

(1 / 3) \cdot 3.14159 \cdot ((\text{ppt\_size}(0) / \sin(chi)) \cdot 3) \cdot (\sin(chi) \cdot 2) \cdot \cos(chi)

determine total volume of ppt
\[ \text{total\_volume}(0) = \text{ppt\_volume}(0) \cdot N_n(0) \]

Return growth:

predictions of precipitate growth

\( \text{equations from Hongs paper} \)

diffusion distance of the solute in the matrix within time \( t \)
\[ \Delta l = \sqrt{2 \cdot D_{vsTa} \cdot t} \]

determine value of \( \Delta l \)

\[ \text{fchi} = ((2 / 3) - \cos(chi) \cdot ((1 / 3) \cdot (\cos(chi) \cdot 3)) / (\sin(chi) \cdot 3)) \cdot 2 \]

\( \text{function of chi} \)

\[ \text{loop\_count} = \Delta l \cdot 1000000000#\]

\[ \text{xai} = \text{results3}(0) \cdot \text{gbw} \cdot \text{Cg} \]

\( \text{for i = 1 to loop\_count} \)
\[ \text{xai} = \text{xai} + (\text{results3}(i) \cdot \text{gbw} \cdot 0.000000001) \]

Next \( i \)

\[ \text{xai} = \text{xai} / \Delta l \]

\( \text{this equation for xai from hongs thesis, page 70} \)

\[ \text{xai} = (\text{xai} - (\text{fchi} \cdot 3.14159 \cdot (\text{ppt\_size}(z - 1) \cdot 3) \cdot (\text{xtheta} - xTage)) / \Delta l \]

\[ \text{store xalphan term in array} \]
\[ \text{xalphai}(z) = \text{xai} \]

\( \text{equation 18 from Hongs paper} \)

\[ \text{Ltop} = (2 \cdot A_m(z - 1) \cdot (D_{vsTa} \cdot 0.5) \cdot (\text{xai} - xTage) \cdot ((t \cdot 0.5) - ((t \cdot \Delta l) \cdot 0.5))) \cdot ralpha \]

\[ \text{Lbottom} = rtheta \cdot (3.14159 \cdot 1.5) \cdot \text{fchi} \cdot (\text{xtheta} - xTage) \]

\( \text{store time and size in arrays} \)
\[ \text{ptt\_time}(z) = t \]
\[ \text{ppt\_size}(z) = ((\text{Ltop} \cdot \text{Lbottom}) + (\text{ppt\_size}(z - 1) \cdot 3)) \cdot (1 / 3) \]

determine volume of one ppt
\[ \text{ppt\_volume}(z) = ((2 / 3) \cdot 3.14159 \cdot ((\text{ppt\_size}(z) / \sin(chi)) \cdot 3) \cdot (1 - \cos(chi))) - ((1 / 3) \cdot 3.14159 \cdot ((\text{ppt\_size}(z) / \sin(chi)) \cdot 3) \cdot (\sin(chi) \cdot 2) \cdot \cos(chi)) \]

determine new collector plate area
\( \text{equation 27 from paper} \)
\[ x = (A_m(z - 1) - A_{min}) / (\sqrt{2} \cdot sdev) \]

\( \text{CoSub erf} \)
erfa = erf(x)

x = (Am(z - 1) - (4 * (ppt_size(z)^2))) / (Sqr(2 * sdev)) 'minus!!!
GoSub erf
erfb = erf(x)

'determine new number of ppt's
Nn(z) = (Nn(z - 1) * (1 - (0.25 * ((erfa - erfb)^2))))

determine total volume of ppt
total_volume(z) = ppt_volume(z) * Nn(z)

determine mean collector plate area from new no. of ppt's
Am(z) = 1 / Nn(z)

Return

coarsening:
equations from Hongs thesis
'total volume of ppts remains constant
'no of ppts decreases
'size of ppts increases
'size of Am increases

g is the number of times the code has run the coarsening routine

\[ g = g + 1 \]

'this determines the value corresponding to where coarsening starts

\[ gtcc = z - g \]

equation 3.4.4 in thesis

\[ bigh = (2 / 3) * (1 - (sigmabb / (2 * sigmabb))) \]

'traction of the grain boundary covered by precipitates
equation 3.4.7 in thesis

\[ f = (3.14159 * (ppt_size(gtcc)^2)) / Am(gtcc) \]

equation 3.4.6 in thesis

\[ B = 0.5 * \log(1 / f) \]

constant in equation 3.4.3 in thesis

\[ \text{bigconst} = (9 * gbw * DbsTa * sigma * xTage * Vtheta) / (32 * \text{bigA} * B * R * Ta) \]

\[ \text{ppt_size}(z) = t \]

'precipitate size during coarsening
equation 3.4.3 in thesis

equation modified as it gave -ve figures, hence sign has been modified

\[ \text{ppt_size}(z) = (-((\text{bigconst} / (5 - (\Delta t + gtcc))) + (\text{ppt_size}(gtcc)^4))^{0.25} \]

'determine volume of one ppt

\[ \text{ppt_volume}(z) = (\{2 / 3\} * 3.14159 * ((\text{ppt_size}(z) / \sin(chi))^{3}) * (1 - \cos(chi))) - ((\{2 / 3\} * 3.14159 * ((\text{ppt_size}(z) / \sin(chi))^{3}) * (\sin(chi) * \cos(chi))) \]

'equation 30 in paper

\[ Am(z) = Am(gtcc) * ((\text{ppt_size}(z) / \text{ppt_size}(gtcc))^3) \]

'equation 29 in paper

\[ Nn(z) = 1 / Am(z) \]

'determine total volume of ppt

\[ \text{total_volume}(z) = \text{ppt_volume}(z) * Nn(z) \]

Return

TaGTmp:
'subroutine for situation where ageing temperature is greater than Tmp
'calculates effective ageing time at Ts using Faulkners equation ref. 4 in paper
'this value is added to hongs effective quenching time at Ts and profile is recalculated
'store segregation profile in array results3

\[ \text{new_teff} = \text{tage} * \exp(-Ea * (Ts - Ta) / (k * Ts * Ta)) \]

\[ \text{teff} = \text{teff} + \text{new_teff} \]
CB = Cb
we = (Cg / CB) * Sqr(2 * DcTs * teff)
wd = 2 * we * (CB - Cg) / Cg
alpha = (2 * 1.14159 * CB ^ 2) / (8 * DcTs * teff * Cg ^ 2)  'DcTs is still used for
temp Ts, uses modified teH to account for ageing time
results3(1) = CB / Cg

For cont = 1 To 500 Step 1
    dist = cont * 0.000000001
    constant = CB * Exp(-alpha * dist ^ 2)
    If dist > we + wd Then CX = Cg + constant
    If dist > we And dist <= we + wd Then CX = ((dist - we) / wd) * Cg + constant
    If dist <= we Then CX = constant
    results3(cont + 1) = CX / Cg
Next cont

Return
End Sub
2-dimensional atomistic simulation

' set up random number generator
Randomize

' check for correct values
GoSub check_val

' set up constants
ebvgb = Text1.Text
ebigb = Text2.Text
ebii = Text3.Text
ebiv = Text4.Text
enigv = Text5.Text
enigi = Text7.Text
alat = Text8.Text
matsiz = Text9.Text
nvac = Text10.Text
ncycle = Text14.Text
FileNumber = Text15.Text

k = 0.0000862 ' Boltzmanns constant (eV/deg K)
oldncycle = 0
enigav = (enigv / 2) + (enigi / 2)

' define ycoord of GB
ygb = matsiz / 2 + 0.5

' define ycoords of adjacent atomic planes
nygb1 = matsiz / 2
nygb2 = nygb1 + 1

' generate random arrays of vacancies and impurities
GoSub gen_vac
GoSub gen_imp

' save generated arrays
GoSub store_gen

' start timer
start = Timer

filesave = 1

'*******************************************************
'** MAIN PROGRAM LOOP TO DO REQUIRED NUMBER OF CYCLES **
'*******************************************************
For npass = 1 To ncycle
    GoSub vacancy_movement
    GoSub impurity_movement
    GoSub remove_vacancies
    If npass = filesave * FileNumber Then
        GoSub some_results
        filesave = filesave + 1
End If
Next npass

'******************************************************************************
'* END OF MAIN PROGRAM LOOP *
'******************************************************************************

'calculate total time
finish = Timer
elapsed = finish - start

'dump final data
pswaps = (swaps / (nvac + nimp)) * 100 / ncycle
ppgt1 = (pgt1 / (nvac + nimp)) * 100 / ncycle

'store results and constants file
GoSub store_res
GoSub constants_output
Exit Sub

gen_vac:
'put vacancies into matrix
If nvac = 0 Then
  'do nothing
Else
  For n = 1 To nvac
    'generate random number between 0 and matsiz
    x = Int(Rnd * matsiz + 1)
    y = Int(Rnd * matsiz + 1)
    'check position not already occupied by vacancy
    For i = 1 To n
      If x = nvacx(i) And y = nvacy(i) Then GoTo 150
    Next
    'store coords
    nvacx(n) = x
    nvacy(n) = y
  Next n
End If

Return

gen_imp:
'put impurity atoms into matrix
If nimp = 0 Then
  'do nothing
Else
  For n = 1 To nimp
    'generate random number between 0 and matsiz
    x = Int(Rnd * matsiz + 1)
    y = Int(Rnd * matsiz + 1)
    'check position not already occupied by an impurity
    For i = 1 To n
      If x = nimpx(n) And y = nimpy(n) Then GoTo 250
    Next i
    'check position not already occupied by a vacancy
    For i = 1 To nvac
      If x = nvacx(i) And y = nvacy(i) Then GoTo 250
    Next i
    'store coords
    nimpx(n) = x
    nimpy(n) = y
  Next n
End If

Return

vacancy_movement:
If nvac = 0 Then Return
For n = 1 To nvac
  'current y position of vacancy
Y1 = nvacy(n)

ignore annihilated vacancies
If Y1 = "" Then GoTo 550

current x position of vacancy
X1 = nvacx(n)

generate possible new position
rand = Int(4 * Rnd + 1)

If rand = 1 Then
    X2 = X1
    Y2 = Y1 - 1
ElseIf rand = 2 Then
    X2 = X1 + 1
    Y2 = Y1
ElseIf rand = 3 Then
    X2 = X1
    Y2 = Y1 + 1
ElseIf rand = 4 Then
    X2 = X1 - 1
    Y2 = Y1
End If

keep new coods between 1 and matsiz (foldover)
If X2 <= 0 Then
    X2 = matsiz
ElseIf X2 >= (matsiz + 1) Then
    X2 = 1
End If
If Y2 <= 0 Then
    Y2 = matsiz
ElseIf Y2 >= (matsiz + 1) Then
    Y2 = 1
End If

is new position occupied by a vacancy
For i = 1 To nvac
    If nvacx(i) < X2 Or nvacx(i) > X2 Then GoTo 420
    If nvacy(i) = Y2 Then GoTo 550 'if x and y coods correspond to vacancy, move
Next i

get binding energy of vacancy in current position (eb1)
Call bind(X1, Y1, ebvv, ebvi, ebvgb, eb1)

get binding energy of vacancy in possible new position (eb2)
Call bind(X2, Y2, ebvv, ebvi, ebvgb, eb2)

is new position occupied by an impurity atom
For i = 1 To nimp
    jmp = 1
    If nimpx(i) < X2 Or nimpx(i) > X2 Then GoTo 440
    If nimpy(i) = Y2 Then GoTo 460
Next i

new position is not occupied by impurity, so energy required for jump, therefore,
e = ((eb1 - eb2 + ebvv) / 2) + emigv

probability of jump being possible
prob = accn * Exp(-e / kT)
If prob > 1# Then pgtl = pgtl + 1

jump will occur if prob > rnd
If Rnd > prob Then GoTo 550

yes, swap coods
swaps = swaps + 1
nvacx(n) = X2
nvacy(n) = Y2

GoTo 550 'skip following lines since these correspond to situation where an
impurity is present

get binding energy of impurity in current position (eb3)
460 Call bind(X2, Y2, ebvi, ebii, ebigb, eb3)

get binding energy of impurity in possible new position (eb4)
Call bind(Xl, Yl, ebvi, ebii, ebigb, eb4)

energy required for jump, therefore,
\[ e = \left( (eb1 - eb2 + eb3 - eb4 + ebvv + ebii) / 2 \right) - ebvi + esigma \]

probability of jump being possible
\[ prob = accn \times \exp(-e / kt) \]
If prob > 1# Then pglt = pglt + 1

jump will occur if prob > rnd
If Rnd > prob Then GoTo 550

yes, swap coords
swaps = swaps + 1
nvacx(n) = X2
nvacy(n) = Y2
nimpx(jimp) = X1
nimpy(jimp) = Y1

550 Next n

Return

impurity_movement:

If nimp = 0 Then Return

For n = 1 To nimp

' current position of impurity
Xl = nimpx(n)
Yl = nimpy(n)

' generate possible new position
rand = Int(4 * Rnd + 1#)
If rand = 1 Then
X2 = Xl
Y2 = Yl - 1
ElseIf rand = 2 Then
X2 = Xl + 1
Y2 = Yl
ElseIf rand = 3 Then
X2 = Xl
Y2 = Yl + 1
ElseIf rand = 4 Then
X2 = Xl - 1
Y2 = Yl
End If

' keep new coords between 1 and matsiz(foldover)
If X2 <= 0 Then
X2 = matsiz
ElseIf X2 >= (matsiz + 1) Then
X2 = 1
End If

If Y2 <= 0 Then
Y2 = matsiz
ElseIf Y2 >= (matsiz + 1) Then
Y2 = 1
End If

' is new position occupied by an impurity
For i = 1 To nimp
If nimpx(i) < X2 Or nimpx(i) > X2 Then GoTo 620
If nimpy(i) = Y2 Then GoTo 750
620 Next i

' get binding energy of impurity in current position(ebl)
Call bind(Xl, Yl, ebvi, ebii, ebigb, ebl)

' get binding energy of impurity in possible new position
Call bind(X2, Y2, ebvi, ebii, ebigb, eb2)
is new position occupied by a vacancy
For i = 1 To nvac
    jimp = i
    If nvacx(i) < X2 Or nvacx(i) > X2 Then GoTo 640
    If nvacy(i) = Y2 Then GoTo 660 'vacancy is present, goto relevant code
640 Next i

no vacancy present - therefore, energy required for jump
e = ((eb1 - eb2 + ebii) / 2) + emigi

probability of jump being possible
prob = acrn * Exp(-e / kt)
If prob > 1# Then pgt1 = pgt1 + 1

does jump occur
If Rnd > prob Then GoTo 750

yes - swap coords
swaps = swaps + 1
nimpx(n) = X2
nimpy(n) = Y2
GoTo 750

get binding energy of vacancy in current position (eb3)
660 Call bind(X2, Y2, ebvv, ebvi, ebvgb, eb3)

get binding energy of vacancy in new position (eb4)
Call bind(X1, Y1, ebvv, ebvi, ebvgb, eb4)

energy required for jump therefore
e = ((eb1 - eb2 + eb3 - eb4 + ebvv + ebii) / 2) - ebvi + emigav

probability of jump being possible
prob = acrn * Exp(-e / kt)
If prob > 1# Then pgt1 = pgt1 + 1

does jump occur
If Rnd > prob Then GoTo 750

yes - swap coords
swaps = swaps + 1
nimpx(n) = X2
nimpy(n) = Y2
GoTo 750

750 Next n

Return

remove_vacancies:
s0 = s0 + 1
If nvaco = 0 Then Return

prob = proba * Exp(probb / s0) / Sqr(s0)

For n = 1 To nvac
    If nvacy(n) = ** Then GoTo 820
    If nvacy(n) < nygb1 Then GoTo 900
    If nvacy(n) > nygb2 Then GoTo 900
    nvacy(n) = **
820 If Rnd > prob Then GoTo 900
830 x = Int(Rnd * matsiz + 1)
y = matsiz
If Rnd < 0.5 Then y = 1

For i = 1 To nimp
    If x = nimpx(i) And y = nimpy(i) Then GoTo 830
Next i

For i = 1 To nvac
    If x = nvacx(i) And y = nvacy(i) Then GoTo 830
Next i
nvacx(n) = x
nvacy(n) = y
900 Next n
Return
End Sub

Static Sub bind(xd, yd, ebv, ebi, ebgb, ebind)
    ebind = 0#
dygb = Abs(ygb - yd)
a = 0.25 / dygb
'binding to vacancies first
If nvac = 0 Then
    'do nothing
Else
    For n = 1 To nvac
        'ignore vacancies that have been annihilated
        If nvacy(n) = 0 Then GoTo 100
        'compute defect separation by pythagoras
        dx = Int(xd - nvacx(n))
dy = Int(yd - nvacy(n))
        'allow for foldover
        If dx > ygb Then dx = matsiz - dx
        If dy > ygb Then dy = matsiz - dy
dsq = dx * dx + dy * dy
        If dsq > 25.1 Then GoTo 100
        If dsq < 0.9 Then GoTo 100
        'summate binding energy
        yv = nvacy(n)
dyvgb = Abs(ygb - yv)
ebind = ebind + ebv * (1 - a / dyvgb) / dsq
    Next n
End If

'binding to impurities next
If nimp = 0 Then
    'do nothing
Else
    For n = 1 To nimp
        'compute defect separation by pythagoras
        dx = Int(xd - nimpx(n))
dy = Int(yd - nimpy(n))
        'allow for foldover
        If dx > ygb Then dx = matsiz - dx
        If dy > ygb Then dy = matsiz - dy
dsq = dx * dx + dy * dy
        If dsq > 25.1 Then GoTo 300
        If dsq < 0.9 Then GoTo 300
        'summate binding energy
        yi = nimpy(n)
dyiogb = Abs(ygb - yi)
ebind = ebind + ebv * (1 - a / dyiogb) / dsq
    Next n
End If

'binding to gb last
If dygb > ygb Then Exit Sub
ebind = ebind + ebgb / (dygb * dygb)
End Sub
3-dimensional atomistic simulation

filenum = FreeFile
Randomize 'set up random number generator
GoSub check_val 'check for correct values

' set up constants
ebvgb = Text1.Text
ebigb = Text2.Text
ebbl = Text3.Text
ebv = Text4.Text
ebvi = Text5.Text
emigv = Text6.Text
emigi = Text7.Text
alat = Text8.Text
matsiz = Text9.Text
nvac = Text10.Text
nimp = Text11.Text
t = Text12.Text
accn = Text13.Text
ncycle = Text14.Text
FileNumber = Text15.Text

k = 0.00000862 'Boltzmanns constant (eV/deg K)
oldncycle = 0
emigav = (emigv / 2) + (emigi / 2)
kt = k * t
pi = 3.1415927

diff = 0.0000018 * Exp(-1.6 / kt)
prob0 = Sqr(diff * accn * 0.00000000001) / matsiz / alat
prob = 2 * prob0 / Sqr(pi)
prob = -0.0625 / prob0 / proba
so = 0

'define ycoord of GB
yg = matsiz / 2 + 0.5

define ycoord of adjacent atomic planes
nygb1 = matsiz / 2
nygb2 = nygb1 + 1

generate random arrays of vacancies and impurities
GoSub gen_vac
GoSub gen_imp

'save generated arrays
GoSub store_gen

start = Timer'start timer
filesave = 1

'*******************************************************
** MAIN PROGRAM LOOP TO DO REQUIRED NUMBER OF CYCLES **
'*******************************************************

For npass = 1 To ncycle
GoSub vacancy_movement
GoSub impurity_movement
GoSub remove_vacancies

'save results every 'filenumber' cycles
If npass = filesave * FileNumber Then
    GoSub some_results
    filesave = filesave + 1
End If
Next npass

'*******************************************************
** END OF MAIN PROGRAM LOOP **
'*******************************************************
'calculate total time
finish = Timer
elapsed = finish - start

'dump final data
pswaps = (swaps / (nvac + nimp)) * 100 / ncycle
ppgt1 = (pgt1 / (nvac + nimp)) * 100 / ncycle

'store results and constants file
GoSub store_res
GoSub constants_output

Exit Sub

gen_vac:
'put vacancies into matrix

If nvac = 0 Then
  'do nothing
Else
  For n = 1 To nvac
    x = Int(Rnd * matsiz + 1)  'generate random number between 0 and matsiz
    y = Int(Rnd * matsiz + 1)
    z = Int(Rnd * matsiz + 1)
    'check position not already occupied by vacancy
    For i = 1 To n
      If x = nvacx(i) And y = nvacy(i) And z = nvacz(i) Then GoTo 150
    Next i
    'store coords
    nvacx(n) = x
    nvacy(n) = y
    nvacz(n) = z
  Next n
End If

Return

gen_imp:
'put impurity atoms into matrix

If nimp = 0 Then
  'do nothing
Else
  For n = 1 To nimp
    x = Int(Rnd * matsiz + 1)
    y = Int(Rnd * matsiz + 1)
    z = Int(Rnd * matsiz + 1)
    'check position not already occupied by an impurity
    For i = 1 To n
      If x = nimpx(n) And y = nimpy(n) And z = nimpz(n) Then GoTo 250
    Next i
    'check position not already occupied by a vacancy
    For i = 1 To nvac
      If x = nvacx(i) And y = nvacy(i) And z = nvacz(i) Then GoTo 250
    Next i
    'store coords
    nimpx(n) = x
    nimpy(n) = y
    nimpz(n) = z
  Next n
End If

Return

vacancy_movement:

If nvac = 0 Then Return

For n = 1 To nvac
  'current y position of vacancy
  Y1 = nvacy(n)
ignore annihilated vacancies
If Y1 == "" Then GoTo 550

' current x position of vacancy
X1 = nvacx(n)

' current z position of vacancy
z1 = nvacz(n)

' generate possible new position
rand = Int(6 * Rnd + 1)

If rand = 1 Then
  X2 = X1
  Y2 = Y1 - 1
  z2 = z1
ElseIf rand = 2 Then
  X2 = X1 + 1
  Y2 = Y1
  z2 = z1
ElseIf rand = 3 Then
  X2 = X1
  Y2 = Y1 + 1
  z2 = z1
ElseIf rand = 4 Then
  X2 = X1 - 1
  Y2 = Y1
  z2 = z1
ElseIf rand = 5 Then
  X2 = X1
  Y2 = Y1
  z2 = z1 + 1
ElseIf rand = 6 Then
  X2 = X1
  Y2 = Y1
  z2 = z1 - 1
End If

' keep new coords between 1 and matsiz (foldover)
If X2 <= 0 Then
  X2 = matsiz
ElseIf X2 >= (matsiz + 1) Then
  X2 = 1
End If

If Y2 <= 0 Then
  Y2 = matsiz
ElseIf Y2 >= (matsiz + 1) Then
  Y2 = 1
End If

If z2 <= 0 Then
  z2 = matsiz
ElseIf z2 >= (matsiz + 1) Then
  z2 = 1
End If

' is new position occupied by a vacancy
For i = 1 To nvac
  If nvacx(i) < X2 Or nvacx(i) > X2 Then GoTo 420
  If nvacy(i) < Y2 Or nvacy(i) > Y2 Then GoTo 420
  If nvacz(i) = z2 Then GoTo 550
Next i

' get binding energy of vacancy in current position (eb1)
Call bind(X1, Y1, z1, ebvv, ebvi, ebvbg, eb1)

' get binding energy of vacancy in possible new position (eb2)
Call bind(X2, Y2, z2, ebvv, ebvi, ebvbg, eb2)

' is new position occupied by an impurity atom
For i = 1 To nimp
  Jimp = 1
  If nimpx(i) < X2 Or nimpx(i) > X2 Then GoTo 440
If nimpy(i) < Y2 Or nimpy(i) > Y2 Then GoTo 440
If nimpz(i) = z2 Then GoTo 460

440 Next i

' new position is not occupied by impurity, so energy required for jump, therefore,
  e = ((eb1 - eb2 + ebv) / 2) + emigv

' probability of jump being possible
prob = accn * Exp(-e / kt)
If prob > 1# Then pgtl = pgtl + 1

' jump will occur if prob > rnd
If Rnd > prob Then GoTo 550

' yes, swap coords
swaps = swaps + 1
nvacx(n) = X2
nvacy(n) = Y2
nvacz(n) = z2

GoTo 550 'skip following lines since these correspond to situation where an
impurity is present

' get binding energy of impurity in current position (eb3)
460 Call bind(X2, Y2, z2, ebvi, ebii, ebigb, eb3)

' get binding energy of impurity in possible new position (eb4)
Call bind(X1, Y1, z1, ebvi, ebii, ebigb, eb4)

' energy required for jump, therefore,
  e = ((eb1 - eb2 + eb3 - eb4 + ebv + ebv) / 2) - ebvi + emigv

' probability of jump being possible
prob = accn * Exp(-e / kt)
If prob > 1# Then pgtl = pgtl + 1

' jump will occur if prob > rnd
If Rnd > prob Then GoTo 550

' yes, swap coords
swaps = swaps + 1
nvacx(n) = X2
nvacy(n) = Y2
nvacz(n) = z2
nimpx(jimp) = X1
nimpy(jimp) = Y1
nimpz(jimp) = z1

550 Next n

Return

impurity_movement:

If nimp = 0 Then Return

For n = 1 To nimp
  ' current position of impurity
  X1 = nimpx(n)
  Y1 = nimpy(n)
  Z1 = nimpz(n)

  ' generate possible new position
  rand = Int(6 * Rnd + 1#)
  If rand = 1 Then
    X2 = X1
    Y2 = Y1 + 1
    Z2 = Z1
  ElseIf rand = 2 Then
    X2 = X1 - 1
    Y2 = Y1
    Z2 = Z1
  ElseIf rand = 3 Then
    X2 = X1
    Y2 = Y1 + 1
    Z2 = Z1
  EndIf
Y2 = Y1 + 1  
z2 = z1  
ElseIf rand = 4 Then  
X2 = X1 - 1  
Y2 = Y1  
z2 = z1  
ElseIf rand = 5 Then  
X2 = X1  
Y2 = Y1  
z2 = z1 + 1  
ElseIf rand = 6 Then  
X2 = X1  
Y2 = Y1  
z2 = z1 - 1  
End If  

' keep new coords between 1 and matsiz(foldover)  
If X2 <= 0 Then  
X2 = matsiz  
ElseIf X2 >= (matsiz + 1) Then  
X2 = 1  
End If  

If Y2 <= 0 Then  
Y2 = matsiz  
ElseIf Y2 >= (matsiz + 1) Then  
Y2 = 1  
End If  

If z2 <= 0 Then  
z2 = matsiz  
ElseIf z2 >= (matsiz + 1) Then  
z2 = 1  
End If  

' is new position occupied by an impurity  
For i = 1 To nimp  
    If nimpX(i) < X2 Or nimpX(i) > X2 Then GoTo 620  
    If nimpY(i) < Y2 Or nimpY(i) > Y2 Then GoTo 620  
    If nimpZ(i) = z2 Then GoTo 750  
620 Next i

' get binding energy of impurity in current position(ebl)  
Call bind(X1, Y1, z1, ebvi, ebl, ebhi, eblg, ebl)  

' get binding energy of impurity in possible new position  
Call bind(X2, Y2, z2, ebvi, ebl, ebhi, eblg, eb2)  

' is new position occupied by a vacancy  
For i = 1 To nvac  
    jimp = i  
    If nvacX(i) < X2 Or nvacX(i) > X2 Then GoTo 640  
    If nvacY(i) < Y2 Or nvacY(i) > Y2 Then GoTo 640  
    If nvacZ(i) = z2 Then GoTo 660  
640 Next i  

' no vacancy present - therefore, energy required for jump  
e = ((ebl - eb2 + eb2i) / 2) + emigi  

' probability of jump being possible  
prob = accn * Exp(-e / kt)  
If prob > 1# Then pgt1 = pgt1 + 1  

' does jump occur  
If Rnd > prob Then GoTo 750  

' yes - swap coords  
swaps = swaps + 1  
nimpx(n) = X2  
nimpy(n) = Y2  
nimpz(n) = z2  
GoTo 750  

' get binding energy of vacancy in current position (eb3)  
660 Call bind(X2, Y2, z2, ebvv, ebvi, ebvgb, eb3)
get binding energy of vacancy in new position (eb4)
Call bind(X1, Y1, z1, ebv, ebvi, ebvgb, eb4)

energy required for jump therefore
$e = ((eb1 - eb2 + eb3 - eb4 + ebv + ebii) / 2) - ebv + emigav$

probability of jump being possible
$prob = accm * \exp(-e / kt)$
If $prob > 1#$ Then $pgt1 = pgt1 + 1$

does jump occur
If $Rnd > prob$ Then GoTo 750

yes - swap coords
swaps = swaps + 1
nimpx(n) = X2
nimpy(n) = Y2
nimpz(n) = z2
nvacx(jimp) = X1
nvacy(jimp) = Y1
nvacz(jimp) = z1

750 Next n

Return

remove_vacancies:
s0 = s0 + 1
If nvac = 0 Then Return

prob = proba * Exp(probb / s0) / Sqr(s0)

For n = 1 To nvac
  If nvacy(n) = "" Then GoTo 820
  If nvacy(n) < nysbl Then GoTo 900
  If nvacy(n) > nysb2 Then GoTo 900
  nvacy(n) = ""
820 If Rnd > prob Then GoTo 900

830 x = Int(Rnd * matsiz + 1)
z = Int(Rnd * matsiz + 1)
y = matsiz
If Rnd < 0.5 Then y = 1

For i = 1 To nimp
  If x = nimpx(i) And y = nimpy(i) And z = nimpz(i) Then GoTo 830
Next i

For i = 1 To nvac
  If x = nvacx(i) And y = nvacy(i) And z = nvacz(i) Then GoTo 830
Next i

nvacx(n) = x
nvacy(n) = y
nvacz(n) = z
900 Next n

Return

End Sub