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MICROSTRUCTURAL EFFECTS OF NEUTRON IRRADIATION ON FERRITIC / MARTENSITIC STAINLESS STEELS

by

TERENCE STUART MORGAN

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

July 1992

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For financial support I am indebted to Loughborough University of Technology for their award of a Research Studentship and to AEA Technology for their supplementation of this; thus allowing me to present some of the initial results in the USA and to visit several National Laboratories there also investigating radiation damage effects in materials. I am also grateful to both organizations for the provision of research facilities.

Sincere thanks must go to my two supervisors, Dr. Roy Faulkner of Loughborough University and Dr. Ted Little of Harwell Laboratory, for their help, advice and encouragement throughout the duration of this work, particularly during the latter stages.

Also at Harwell Laboratory, in addition to recognizing the help of the authority as a whole, are several other individuals to whom I owe particular thanks: Derrick Stow for general instruction and guidance in the techniques for radioactive material handling and specimen preparation; Will Fuller for similar advice and practical help in the preparation of the reduced-activity thin foil specimens for microanalysis; Dr. John Titchmarsh for tuition on the operation of the VG HB501 FEGSTEM in particular and for discussions concerning microanalytical techniques and transmission electron microscopy in general; and lastly, Ian Vatter and Simon Dumbill for similar advice concerning microanalysis and spectrum quantification.

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Abstract

Neutron irradiation generates point defect fluxes to sinks such as grain boundaries and dislocations; such fluxes may promote net solute redistribution via radiation-induced segregation, leading to microalloyed regions adjacent to sinks in nuclear reactor core structural materials. The effects that such changes may exert on local precipitation and boundary-sensitive properties can be profound.

A commercial grade 12%CrMoVNb ferritic/martensitic stainless steel in the form of parent plate and high-nickel off-normal weld material has been fast neutron irradiated to equivalent damage levels of 33 and 50 dpa at 400 and 465°C respectively. The microstructural and microchemical changes induced in the irradiated material, together with as-tempered and thermal control material, have been determined to high resolution by conventional transmission electron microscopy and the use of a field emission gun scanning transmission electron microscope (FEGSTEM).

Equilibrium (co)segregation of chromium, molybdenum and phosphorus was detected at boundary planes in thermally aged material, with greater enrichment at the higher ageing temperature. The relative magnitudes of apparent phosphorus segregation at the two temperatures were in accordance with McLean's model governing the kinetic approach to equilibrium. The electron probe/ segregant interaction was modelled in an attempt to deconvolute true segregant concentrations from derived concentration profiles: these 'deconvoluted' concentrations approximated those predicted by McLean's model.

The net effects of irradiation on parent plate interfacial microchemistry were found to be: (i) inhibit the (co)segregation of chromium, molybdenum and phosphorus, (ii) cause chromium depletion from adjacent to boundary planes, (iii) cause enrichment of silicon at prior austenite and lath boundaries during irradiation at 400°C and (iv) cause enrichment of nickel at lath boundary planes only, at both temperatures. The radiation-induced precipitates \( \text{M}_{23} \) and G phase, both nickel- and silicon-rich, were observed.

The fully martensitic off-normal weld metal transformed to a duplex austenite/ferrite structure during irradiation at 465°C; in contrast the thermal control was at least metastable. The transformation was thought to be a martensitic reversion, facilitated by radiation-generated dislocation loops acting as nucleation sites. The austenite was heavily voided (~15 vol.%); the ferrite was relatively void-free. Depletion of the oversized solutes chromium, manganese and molybdenum and enrichment of nickel, silicon, aluminium and traces of titanium were detected at void interfaces in the austenite: little segregation could be discerned at voids in the ferrite.

Overall, the results within this work and in comparison to previous studies highlight the sensitivity to initial composition, microstructure and heat treatment that the 12%Cr ferritic/martensitic steels display in their response to irradiation.
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CHAPTER ONE
Introduction

Two of the major long-term aims of future nuclear power generation strategy are the successful commercial implementation of (i) the fast breeder reactor (FBR) and (ii) ultimately the fusion reactor, probably based on a magnetically confined tokomak design. Neutron irradiation damage to structural components in both reactor designs will accrue at a faster rate than for present conventional nuclear power plant and, crucially, to far higher total damage levels. Consequently end-of-life displacement damage levels of the order of 500 dpa* are projected for the first wall of certain advanced fusion reactor designs for commercial operation [1]. Such high levels of displacement damage place severe constraints on material selection for core components in fast breeder reactors and the first wall of fusion reactor designs. The development of materials to successfully withstand these levels of displacement damage is as necessary a problem to solve as the physics of reactor operation.

Ferritic/martensitic stainless steels have emerged as leading candidate structural materials to meet these high damage level applications [3,4]. The selection of this class of materials is based primarily on their high resistance to the phenomenon of void swelling. Most materials when neutron irradiated at intermediate temperatures, between about 0.3 and 0.6T_m, exhibit an approximately linear volume increase with increasing displacement damage after a certain incubation period. This volume increase is caused by the radiation-induced formation and subsequent growth of internal voids in the material, the phenomenon known as void swelling. Materials can thus "fail" in service simply by not meeting dimensional requirements after volume increases caused by swelling, aside from any other effects the voids impart on material properties. Different materials show differing swelling rates after varying incubation doses, as shown graphically in Figure 1.1 [5]. The commercial ferritic steels, typically based on a composition of 12%Cr 0.1%C with other minor solute additions, require a larger incubation damage level and exhibit a much reduced swelling rate thereafter, compared with the austenitic class of materials: hence their attractiveness.

* [Displacements per atom (dpa) is the usual index of radiation exposure, correlating levels of damage to materials. It is a measure of the average number of times an atom is displaced from its lattice site during the irradiation period. For neutron irradiations the dpa is based on the energy spectrum and an energy-dependent cross section for the material in question. It was originally intended to be a measure of the number of stable point defects created at low temperature, that is, below stage 1 annealing.] [2]
Figure 1.1: Swelling of several classes of steel as a function of neutron dose, irradiated in EBR-II in the temperature range 450 to 550°C [5].
A further, more recently discovered consequence of displacement damage in materials subject to irradiation is radiation-induced segregation. This phenomenon of non-equilibrium solute transport also occurs at the intermediate temperatures typical of fast breeder and fusion reactor operations. Radiation-induced segregation causes compositional modifications at point-defect sinks such as grain boundaries, dislocations, precipitate interfaces and void surfaces. Even slight modifications to grain boundary chemistry may result in the gross alteration of boundary-sensitive bulk material properties such as fracture toughness. Solute segregation under the action of irradiation is also thought to influence the development of unexpected phases observed in irradiated materials. Void swelling in irradiated ferritic materials has also recently been cited as being controlled by solute segregation \(^6\). However, no mechanism was put forward owing to the lack of experimental observations of radiation-induced segregation in ferritic materials. Some models describing radiation-induced segregation have been developed, but the critical input parameters are generally poorly known. Furthermore, the models have usually been derived for binary or ternary alloys, with assumptions limiting their applicability for technological materials. Therefore, the principal aim of the work described in this thesis was to investigate experimentally the effects of high dose neutron irradiation on the interfacial microchemistry of commercial ferritic/martensitic stainless steel parent plate and weld material.

Since neutron irradiation to high displacement damage levels involves holding the material at elevated temperature for a considerable time, the resultant interfacial microchemistry and microstructural development is modified conjointly by thermal and irradiation effects. Consequently the following chapter on theory and previous work begins with an outline of the conventional physical metallurgy of 12\%Cr steels and the microstructural and microchemical changes brought about by purely thermal treatments. The irradiation damage process is then described with the possible mechanisms for consequent modification of interfacial microchemistry reviewed. The physical basis of the particular mechanism of radiation-induced segregation is then dealt with in detail, followed by a review of its experimental observation in ferritic materials. Chapter Three sets out the experimental procedures carried out in this study, and Chapter Four reports the results of these procedures. Chapter Five discusses the interpretation of the results obtained and finally the main conclusions are set out in Chapter Six.
2.1 The 12%Cr steels

2.1.1 Introduction

The generic 12%Cr steels are an important class of materials, combining corrosion and high temperature oxidation resistance with good mechanical properties. The relatively complex physical metallurgy of these steels allows the final mechanical properties to be tailored to meet specific demands. A brief review of the relevant physical metallurgy will be presented here: general reviews of the physical metallurgy of 12%Cr steels are given by Pickering [7] and Irvine et al [8], specific reviews of the metallurgy of candidate 12%Cr steels for reactor use are also available [9-12].

2.1.2 Constitution

As noted in the introduction, these steels have a typical base composition of 12%Cr 0.1%C with additional alloying elements present generally at concentrations of less than 1%. The 12%Cr section of the Fe-Cr-C ternary phase diagram is shown in Figure 2.1 [7]; the 0.1%C section in Figure 2.2 [7]. The single phase austenite region is the most important in terms of heat treatment and thus final mechanical properties. In order to achieve a fully martensitic structure on cooling from the austenitizing temperature, and hence the highest possible strength prior to tempering: (i) the steel must be fully austenitic at that temperature, (ii) the martensite transformation temperatures, $M_s$ and $M_f$, must be sufficiently high to ensure complete martensitic transformation at room temperature and (iii) the cooling rate must be rapid enough to prohibit the pearlite and bainite reactions.

It can be seen from Figures 2.1 and 2.2 that the composition Fe-12%Cr-0.1%C lies close to the edge of the austenite phase field over the usual austenitizing temperature range of 950-1100°C. The region of austenite stability can be increased by the addition of austenite forming elements (C, N, Ni, Mn or Co) or a decrease in the ferrite forming elements (Cr, Si, Mo, W, V, Al, Ti, Nb, etc.). The relative efficiency of elements to stabilize austenite or ferrite are given in terms of nickel or chromium equivalents respectively, as follows [13]:

\[
\begin{align*}
\text{Ni}_{eq} &= \%\text{Ni} + \%\text{Co} + 30(\%\text{C}) + 25(\%\text{N}) + 0.5(\%\text{Mn}) + 0.3(\%\text{Cu}) \\
\text{Cr}_{eq} &= \%\text{Cr} + 2(\%\text{Si}) + 1.5(\%\text{Mo}) + 5(\%\text{V}) + 5.5(\%\text{Al}) + 1.75(\%\text{Nb}) + 1.5(\%\text{Ti}) + 0.75(\%\text{W})
\end{align*}
\]
Figure 2.1: The 12%Cr section of the Fe-Cr-C ternary system [7].

Figure 2.2: The 0.1%C section of the Fe-Cr-C ternary system [7].
The transition metal ferrite formers are particularly effective since they are also strong carbide formers, scavenging both carbon and nitrogen from solid solution to form very stable sparingly soluble carbides and nitrides. For this reason, they are often added to increase the high temperature strength and creep resistance of these steels. Consequently, if a fully austenitic structure is to be obtained at the solution treatment temperature, small additions of austenite formers - usually nickel or manganese - have to be made. The compositions of several classes of commercial grade 12%Cr steels are listed in Table 1 [3,4].

The transformation of austenite to martensite on cooling occurs by a diffusionless shear reaction, in which the martensite product has a particular crystallographic orientation relationship with the parent austenite, dependent upon composition. The transformation commences at a well-defined temperature, \( M_s \), and continues as the temperature falls to \( M_f \), when the reaction is complete. The martensite transformation temperatures, \( M_s \) and \( M_f \), are a linear function of composition [14,15]: all solute additions, with the exception of cobalt, acting to depress the \( M_s \) temperature. The relative effects of solute additions on the \( M_s \) temperature have been determined empirically, for example [16,17]:

\[
M_s \ (°C) = 539 - 423(°C) - 30.4(°Mn) - 17.7(°Ni) - 12.1(°Cr) - 7.5(°Mo) - 7.5(°Si) + 10(°Co)
\]

Thus, the \( M_s \) temperature for a 12%Cr 0.1%C steel is depressed to near 300°C, as shown by the values given for the commercial grade 12%Cr steels in Table 2 [18]. Since the martensite transformation temperature range is approximately 150°C the \( M_f \) temperature is in the region of 150°C, Table 2. Hence complete transformation is possible by cooling to room temperature at the appropriate rate.

The addition of even small quantities of substitutional alloying elements significantly retards the pearlite reaction and depresses the bainite reaction to lower temperatures. The austenite formers nickel and manganese act to depress the \( A_f \) temperature, hence reducing the thermodynamic driving force for the pearlite reaction at any given temperature [19]. Carbide forming elements increase the \( A_f \) temperature, but since alloy partitioning occurs over the entire range of pearlite formation, the drastic reduction in pearlite growth rate has been attributed to solute drag and partitioning of strong carbide formers [20,21]. This suppression of the pearlite and bainite reactions is clearly seen when examining the isothermal transformation diagram for a representative 12%Cr steel, as shown by Figure 2.3 [22]. Consequently, the 12%Cr steels possess high hardenability - being air hardenable, even in large section.
Table 1

Typical compositions of 10-12%Cr martensitic steels for fast and fusion reactor applications [3,4].

<table>
<thead>
<tr>
<th>Steel type</th>
<th>Designation</th>
<th>Composition (wt.%)</th>
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<tr>
<td></td>
<td></td>
<td>C  Si  Mn  Cr  Ni  Mo  V  Nb  Other</td>
<td></td>
</tr>
<tr>
<td>12%Cr</td>
<td>FI</td>
<td>0.10 0.18 0.41 12.10 0.49</td>
<td>UK</td>
</tr>
<tr>
<td>12%CrMo</td>
<td>IKH12M252</td>
<td>0.15 1.80 0.40 12.70 0.20 1.60</td>
<td>USSR</td>
</tr>
<tr>
<td>12%CrMoV</td>
<td>FV607</td>
<td>0.13 0.40 0.77 11.16 0.62 0.89 0.32</td>
<td>UK</td>
</tr>
<tr>
<td></td>
<td>CRM12</td>
<td>0.19 0.45 0.54 11.80 0.96 0.30</td>
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<td>0.21 0.37 0.50 11.20 0.42 0.83 0.21</td>
<td>Germany</td>
</tr>
<tr>
<td></td>
<td>HT-9</td>
<td>0.20 0.38 0.59 11.95 0.62 0.99 0.30</td>
<td>USA</td>
</tr>
<tr>
<td>12%CrMoVNb</td>
<td>FV448</td>
<td>0.10 0.46 0.86 10.70 0.65 0.60 0.14 0.26</td>
<td>UK</td>
</tr>
<tr>
<td></td>
<td>EM12</td>
<td>0.10 0.30 0.75 11.90 0.60 1.70 0.25 0.25</td>
<td>France</td>
</tr>
<tr>
<td></td>
<td>JFMS</td>
<td>0.056 0.74 0.60 9.80 1.00 2.40 0.12 0.06</td>
<td>Japan</td>
</tr>
<tr>
<td></td>
<td>1.4914</td>
<td>0.11 0.45 0.35 11.30 0.70 0.50 0.30 0.25</td>
<td>Germany</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2

Ferrite / austenite transformation temperatures ($A_C_1$ and $A_C_2$) and austenite / martensite transformation temperatures ($M_s$ and $M_f$) for representative 12%Cr steels [18].

<table>
<thead>
<tr>
<th>Steel designation</th>
<th>Transformation temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_C_1$</td>
</tr>
<tr>
<td>FI</td>
<td>820</td>
</tr>
<tr>
<td>FV607</td>
<td>780</td>
</tr>
<tr>
<td>FV448</td>
<td>800</td>
</tr>
</tbody>
</table>
Figure 2.3: Isothermal transformation diagram for a representative 12%Cr steel [22].
Thus, the constitution of the microstructure formed after cooling depends upon the composition of the steel and the austenitizing temperature. A commonly used indicator of microstructure formed after cooling is the Schaeffler diagram - originally developed for predicting weld zone microstructures [23]. The nickel and chromium equivalents, defined above, form the ordinate and abscissa, respectively, of a constitution diagram as illustrated by Figure 2.4 [24]. The 12%Cr steels lie primarily within the martensite region, extending slightly into the two phase martensite and ferrite region, as indicated. The as-cooled microstructure of these steels then consists of a network of prior austenite grain boundaries, containing packets of heavily dislocated lath martensite. The laths are very long and approximately 0.5 μm in width with low angle boundaries separating each lath. Films of retained austenite may be present between the martensite laths - specifically in steels with low $M_s$ temperatures. There is also the possibility of delta ferrite being retained in the microstructure - particularly in weld metal zones.

### 2.1.3 Tempering

In order that the steel should possess a useful combination of strength, toughness and ductility, the as-cooled martensite must be reheated to a suitable temperature below $A_1$, i.e. tempered. Significant microstructural changes occur during tempering, which ultimately determine the mechanical properties of the steel in service. Despite the negligible solubility of carbon in ferrite, Figure 2.1, almost all the carbon is retained in supersaturated solid solution in virgin martensite. Tempering is thus essentially an ageing process in which precipitation occurs in several stages. Reviews of the tempering of ferrous martensites are readily obtainable [24-26]; literature specific to the tempering of 12%Cr steels is also available [8,10,27]. Briefly, the effects of tempering may be summarized by a schematic tempering curve, showing the variation of hardness with tempering temperature, as illustrated in Figure 2.5.

As noted above, almost all the carbon is held in supersaturated solid solution in as-cooled martensite. However, the relatively high $M_s$ temperatures of the 12%Cr steels can result in slight precipitation of small particles of $(\text{Fe,Cr})_3\text{C}$ at dislocations in the lath structure, arising from autotempering during cooling. Tempering at temperatures up to 400°C produces little change apart from an increase in the number of $(\text{Fe,Cr})_3\text{C}$ precipitates within the laths. Chromium, along with other ferrite forming elements, increases the stability of the supersaturated iron-carbon solid solution. This preserves the tetragonality of the lattice to 450-500°C, as compared with 250-300°C in plain carbon steels.

At tempering temperatures of 450-500°C, fine matrix precipitation occurs. This is mainly $\text{Cr}_7\text{C}_3$ formed by separate nucleation and growth, but there is also an in situ
Figure 2.4: Schaeffler diagram predicting the constituent phases present in steels following rapid cooling after welding, as a function of chromium and nickel equivalents, with the approximate compositional region of the 12%Cr steels marked, after [24].

Figure 2.5: Schematic tempering curve, showing variation in hardness with tempering temperature and the corresponding microstructural changes.
transformation of (Fe,Cr)$_3$C to Cr$_7$C$_3$; chromium diffusion causes nucleation of Cr$_7$C$_3$ at the cementite/ferrite interface with carbon being supplied by the dissolution of adjacent cementite. In addition, in those steels containing alloying elements such as Mo, V or Nb and N, the fine needle-like M$_2$X phase also forms. This fine matrix precipitation, particularly of the M$_2$X phase, is responsible for the slight increase in hardness in these steels after tempering at 450-500°C - so called 'secondary hardening'. The greater the amount of Mo, V or Nb dissolved in the M$_2$X, the higher the temperature at which it forms and thus the slower the rate at which it overages.

Increasing the tempering temperature still further to above 500°C results in the nucleation of carbide particles at martensite lath and prior austenite grain boundaries. This boundary precipitate is M$_{23}$C$_6$, and as tempering proceeds begins to coarsen at the expense of Cr$_7$C$_3$. Rapid overaging occurs as the dissolution of Cr$_7$C$_3$ and ultimately M$_2$X at still higher temperatures allows dislocations to anneal out, forming polygonized networks. Tempering at 750°C causes growth of subcells within laths to fairly equiaxed subgrains with large inter- and intragranular M$_{23}$C$_6$. There is little evidence of the original lath structure and virtually all the hardness associated with the martensite has been lost.

The variation in mechanical properties of 12%Cr steels reflect the microstructural changes that occur during tempering. The effect of tempering temperature on the hardness of three 12%Cr steels and the effect of their minor alloying additions is shown in Figure 2.6 [10]. Referring to Table 1, FI steel is a plain 12%Cr 0.1%C steel; FV607 has additions of Mo and V to increase temper resistance; whilst FV448 has additions of Mo, V and Nb. There is a slight increase in hardness with tempering temperature up to 500°C, being more pronounced in the case of FV448, corresponding to the precipitation of M$_2$X/Cr$_7$C$_3$. Above 500°C the onset of overaging occurs as M$_{23}$C$_6$ begins to form at the expense of M$_2$X and Cr$_7$C$_3$, causing a rapid fall in hardness with increasing tempering temperature. The effect of niobium in particular on retarding the onset and extent of softening in the case of FV448 can be seen.

The changes in hardness are mirrored in Figure 2.7 [10], illustrating the variation in tensile properties with tempering temperature. Again, the niobium stabilized FV448 is the most resistant to tempering. In contrast, both FI and FV607 steels show a marked increase in ductility on raising the tempering temperature from 700 to 750°C. This coincides with the decrease in dislocation density, polygonization and the destruction of the lath morphology of the prior martensite in these steels - which the niobium stabilized steel retains to higher temperatures.
Figure 2.6: The variation in hardness of three 12%Cr steels, having differing alloying contents, as a function of tempering treatment temperature [10].
Figure 2.7: The effect of tempering treatment temperature on the tensile properties of four 12% Cr steels having differing alloying content [10].
2.1.4 Thermal microchemical effects

Aside from the precipitation and recovery effects of tempering described above, heat treatment variables may affect the microchemistry in other, usually less desirable, ways. Segregation to point defect sinks, such as dislocations, precipitate interfaces and grain and lath boundaries is possible by one or both of two distinct mechanisms: equilibrium and non-equilibrium segregation. Quenched and tempered martensitic steels may exhibit characteristics from both these mechanisms. Further microchemical change may occur during long term thermal ageing. These three factors will be discussed below, with particular attention paid to results pertaining to 12%Cr steels.

2.1.4.1 Equilibrium segregation

The phenomenon of the equilibrium segregation of dilute solutes to interfaces has been recognized for some time, since the work of Gibbs [28]. The driving force for equilibrium segregation to surfaces, grain boundaries and other interfaces is the minimization of a system's free energy: hence 'equilibrium' segregation. There will be a reduction in free energy if a solute atom and its associated strain energy is transferred from the matrix to a strain-free environment at an interface. For a free energy change of $E_b$ for a solute at a concentration of $C_g$ in the matrix at a temperature $T$, the equilibrium interface concentration, $C_b$, is given by [29]:

$$C_b = \frac{C_g \exp \left( \frac{E_b}{kT} \right)}{1 + C_g \exp \left( \frac{E_b}{kT} \right)}$$

This is the interfacial concentration at equilibrium; the true interfacial concentration will be diffusion-controlled and hence will vary with time, as initially modelled by McLean [29]. The lower the temperature the greater the equilibrium concentration of a solute at an interface, but also the longer the time required for equilibrium to be achieved. Consequently, equilibrium segregation tends to be of most concern at intermediate temperatures.

A further important feature of equilibrium segregation is that its spatial distribution is confined to the atomic layer immediately adjacent to the interface; that is, where solute strain energy relief can occur. Thus equilibrium segregation is often described in terms of fractional monolayer coverage. Several reviews of the theory, detection and effects of equilibrium segregation are available in the literature [30-33]. Considerable effort has been made, particularly by Guttman and co-workers, on the thermodynamics and observation
of interactive cosegregation [34-36]. This phenomenon is thought particularly important in its role in the temper embrittlement of martensite [37,38].

Temper embrittlement [39-42] is characterized by a loss of toughness, an upward shift in ductile to brittle transition temperature and a change from transgranular to intergranular fracture. It occurs when tempered alloy steels have been heated in the temperature range 350-600°C, and is reversible. It is known to be caused by segregation of phosphorus (and other elements such as S, Sn, Sb, Se, As) to prior austenite grain boundaries. The segregation of these tramp elements to interfaces can be enhanced or inhibited, and their effect there modified, by metallic solute elements. Indeed, it has been shown that even impure plain carbon steels do not appear susceptible to temper embrittlement - the presence of at least one transition metal element (Cr, Mn, Ni, etc.) at a concentration of greater than about 0.5% was found to be necessary [43].

Guttman [34] showed that if two solutes have a stronger attraction for each other than either has for the solvent, then this will enhance the segregation of both solutes at the boundary. However, if the interaction is very strong then bulk scavenging takes place, thus reducing any such cosegregation by reducing the matrix impurity concentration. In ternary Fe-M-I systems (where M is a transition metal solute and I a residual non-metallic element) analysis of the thermodynamic interactions is reasonably straightforward. However, in more complex alloys, such as real engineering materials, the situation is more complicated with both synergistic and competitive effects. In particular, the role of carbon is convoluted as, for example, the large Mo-C interaction drags molybdenum to the boundaries which in turn attracts phosphorus owing to the large Mo-P interaction; but the segregation of phosphorus is strongly opposed by the competitive site action of carbon since there is a large, repulsive P-C interaction [36]. Thermodynamic analysis reveals that the interaction energy between phosphorus and an alloying element M increases in the order Ni, Mn, Cr, Mo [36].

Results from work carried out on 12%Cr martensitic steels reveal strong evidence for the cosegregation of phosphorus with chromium and molybdenum and possibly nickel and manganese [44-46]. Lemble et al [44] aged a 12%CrNiMoV steel at 540°C for 2 hours after an austenitization and tempering treatment. Auger electron spectroscopy of fracture surfaces revealed segregation of phosphorus, chromium and nickel to the prior austenite grain boundaries at which fracture occurred. Guillou et al [45] investigated three 12%Cr steels with increasing concentrations of molybdenum: 0.10, 0.47 and 0.98 wt.% respectively. Ageing was carried out at 500, 550, 600 and 650°C. Phosphorus, chromium, molybdenum and nickel were all found to be segregated to boundaries fractured and analysed via Auger electron spectroscopy. The maximum phosphorus
Figure 2.8: Temperature dependence of maximum (steady-state) segregation of phosphorus for three 12%Cr steels with varying bulk molybdenum concentrations [45].
fraughtured and analysed via Auger electron spectroscopy. The maximum phosphorus segregation was found to increase with decreasing ageing temperature, but also the time to reach peak segregation increased with decreasing temperature: taking 250 hours at 500°C whilst only 2 hours at 650°C. This leads to the conclusion that the segregation is, indeed, equilibrium segregation. Increasing the molybdenum content was found to decrease the intergranular phosphorus concentration, as illustrated in Figure 2.8, by reducing the solubility of phosphorus in the matrix. Edwards and Little [46] also used Auger electron spectroscopy to determine intergranular composition in a molybdenum-free 12%Cr steel after ageing at temperatures between 450 and 750°C. Intergranular fracture occurred after treatment at between 500 and 650°C. They too always found that the intergranular fracture facets were associated with phosphorus segregation and an enhancement of chromium relative to the matrix.

It should perhaps be mentioned that the phenomenon of interactive cosegregation has not received universal acceptance. Erhart and Grabke [47] have shown that chromium does not increase phosphorus segregation in a low carbon Fe-P alloy and that the addition of carbon, which is surface active, to an Fe-P alloy decreases phosphorus segregation by a site competition mechanism. Furthermore, although chromium does produce increased phosphorus segregation in an Fe-P-C alloy, it does so only indirectly by the formation of chromium-rich carbides, thereby reducing the boundary carbon activity. Briant [48] has shown that additions of between 1.7 and 6.6%Cr to a 3.5Ni-0.3C steel containing 0.06%P did not increase the level of phosphorus segregation. Lee et al [49] have also shown that grain boundary phosphorus segregation was unaffected by additions of several wt.% of manganese, molybdenum or tungsten to iron containing 0.1%P and about 100 ppm C.

2.1.4.2 Non-equilibrium segregation

Non-equilibrium segregation has only more recently come to attention. It was first inferred by Westbrook [50] from grain boundary hardness measurements. In contrast to the thermodynamic equilibrium segregation, non-equilibrium segregation is kinetically driven. The equilibrium vacancy concentration, \( C_v \), is an exponential function of temperature, viz:

\[
C_v = A \exp\left(\frac{-E_f}{kT}\right)
\]

where \( A \) is a geometrical constant, \( E_f \) the vacancy formation energy and \( T \) the absolute temperature. On cooling from a high temperature the equilibrium vacancy concentration
falls, causing instantaneous vacancy concentration gradients adjacent to point defect sinks, such as grain boundaries, where annihilation preserves the equilibrium concentration. Solute atoms in the matrix have an associated strain energy, which may be partly relieved by pairing the solute atom with a vacancy. This solute-vacancy binding energy causes any vacancy flux to have a coupled solute flux. Hence, on cooling at an appropriate rate, solute segregation to point defect sinks may result. The effect of critical temperature and cooling rate are shown schematically in Figure 2.9 [31]. At low cooling rates homogenization of vacancy or solute concentration is possible; at high cooling rates insufficient time prevents solute-vacancy complex diffusion taking place; at low initial temperatures the equilibrium vacancy concentration is too low and the kinetics too slow for appreciable segregation to arise. Hence, non-equilibrium segregation occurs on cooling at intermediate rates from high temperature, such as oil quenching or air cooling thin sections from austenitizing treatment temperatures.

Important differences between the distinguishing features of non-equilibrium and equilibrium segregation exist. First, the spatial extent of the segregant is not confined to an interfacial monolayer as is the case for equilibrium segregation; instead solute redistribution may extend to hundreds of atomic layers for non-equilibrium segregation. Second, non-equilibrium segregation becomes greater with increasing temperature, in contrast to equilibrium segregation. Finally, thermal ageing will eventually homogenize non-equilibrium segregation, since by definition it is non-equilibrium; whereas ageing increases equilibrium segregation as the system approaches equilibrium with time. For further details concerning vacancy current generated non-equilibrium segregation, see ref's [31,51,52]; models quantifying non-equilibrium segregation and linking it with equilibrium segregation are also available [53-55]. A stumbling block to the application of such models is the lack of detailed parameters such as vacancy-solute binding energies which are critical to the models' success.

Non-equilibrium segregation has been experimentally determined in a ferritic steel by Doig and Flewitt [56]. They austenitized a 2\%Cr steel at two different temperatures and water quenched to a martensitic structure. Chemical compositions on and off prior austenite grain boundaries were determined via energy dispersive X-ray analysis using a conventional scanning transmission electron microscope (STEM). Significant boundary chromium segregation was detected, being slightly greater after cooling from the higher temperature.

Druce [57] used Auger electron spectroscopy to find non-equilibrium phosphorus segregation in an MnMoNi steel following austenitization at temperatures between 850
Figure 2.9: Schematic diagram showing the limits of initial temperature and quench rate beyond which appreciable non-equilibrium segregation ceases to occur [31].
The magnitude of the phosphorus segregation increased with increasing austenitization temperature.

Some evidence of non-equilibrium segregation in a 12%Cr steel has been reported by Adetunji [58]. Specimens of the 12%CrMoVNb steel DIN 1.4914 were air cooled, oil quenched or water quenched from a fixed austenitizing temperature, giving cooling rates of 6.5, 50 and 220°C s⁻¹ respectively. Thin foil specimens were examined using the Harwell VG HB501 field emission gun scanning transmission electron microscope (FEGSTEM), for details of which see Section 3.6.1. Spatial chemical composition was determined by energy dispersive X-ray analysis across lath boundaries. Mean segregation profiles were constructed from only those boundaries showing significant segregation. Silicon was cited as the principal segregant, with some indications of molybdenum and nickel segregation reported. The magnitude of segregation was found to be dependent upon the cooling rate: the greatest magnitude of silicon segregation was found after oil quenching, as shown by Figure 2.10. However, segregation was detected across by far the fewest lath boundaries in this condition: 17% as compared with 38% and 75% for the water quenched and air cooled conditions respectively. Adeutunji claims cosegregation of molybdenum and silicon because the maximum segregation of both elements is found after oil quenching. However, the variation of their segregation profiles with quench rate, as illustrated in Figures 2.10 and 2.11, are dissimilar. Analysis of his results, however, indicates the possible cosegregation of chromium and molybdenum and perhaps vanadium, as demonstrated in Figure 2.12. No measurements of any phosphorus segregation were made.

2.1.4.3 Thermal ageing

Microstructural changes during thermal ageing are usually driven by solute supersaturation and diffusion, together with dislocation and boundary recovery processes. However, a tempered microstructure ought to be resistant to recovery during ageing at temperatures below the tempering temperature.

The most significant microstructural change observed when ageing 12%Cr steels containing molybdenum is the formation of Laves phase. The Laves phase in steels is a hard brittle intermetallic compound based on the composition Fe₂Mo and isomorphous with the hexagonal MgZn₂ structure. Laves phase has variously been reported after ageing studies of molybdenum-containing 12%Cr steels at temperatures between approximately 500 and 700°C [59-64]. Stoter and Little [60] observed the phase after ageing FV448 for 8250 hours at 600°C, but not at 460°C. They reported its composition as 42Fe-25Mo-16Cr-10Si-4P-1.5Mn-1Ni. Maziasz and Klueh [61] observed the phase at
Figure 2.10: The variation of silicon concentration with distance from lath boundaries in DIN 1.4914 cooled at three different rates from 1050°C [58].

Figure 2.11: The variation of molybdenum concentration with distance from lath boundaries in DIN 1.4914 cooled at three different rates from 1050°C [58].
Figure 2.12: Solute concentration profiles across lath boundaries in DIN 1.4914 water quenched from 1050°C, data from ref.[58].
all ageing temperatures in the range 482 to 593°C in a 9Cr1MoVNb steel, the phase composition being very similar to that of Stoter and Little. Chen and Wilcox [62] observed the phase at ageing temperatures between 500 and 700°C in HT9, as did Hosoi et al. [63] in a 9%Cr 2%Mo steel. Vatter and Titchmarsh [64] found the phase in a 9%Cr-1%Mo steel aged at 550°C. The morphology of the phase is important; it tends to form as intergranular sheets primarily at prior austenite grain boundaries but also along lath boundaries and as a crust surrounding $M_{23}C_6$ particles. It has a deleterious effect on impact toughness and stress corrosion.

Laves phase stability is determined by relative atomic radii and average electron concentration [65]. Silicon acts to reduce the electron concentration [66] and is also reported to decrease the stability of molybdenum in ferrite [67] thus stabilizing Laves phase. The effect of silicon concentration on the precipitation behaviour of Laves phase has been demonstrated by Hosoi et al. [63], illustrated in Figure 2.13: Laves formation is clearly inhibited in the silicon-free steel. Conversely, Laves formation is thought to be inhibited by the presence of carbon, such that its formation is effectively enhanced in carbon depleted zones [68,69].

Additional microstructural changes found during ageing of 12%Cr steels are the coarsening of $M_{23}C_6$, complete dissolution of $M_2X$ and the formation of fine needle-like intragranular MX precipitates [60-62]. These MX are found after ageing in the same temperature regime as Laves phase, 500 to 700°C, and are vanadium and chromium rich.

2.1.5 Summary

From the above it is clear that the structure and microchemistry of the 12%Cr martensitic steels are complicated by thermal treatments received before and during service. The start of service condition for these materials is usually quenched and tempered. That is, a rapid cool from a high temperature (austenitizing) followed by short term ageing at an intermediate temperature (tempering) and a further cool. Thus, even if the quench from austenitizing is too rapid to allow non-equilibrium segregation during cooling, there will be a frozen-in vacancy superaturation. The subsequent heat treatment causes these vacancies to diffuse to point defect sinks together with any coupled solute flux. Superimposed upon this non-equilibrium segregation will be any relevant equilibrium segregation for this time at temperature. An example of the combination of equilibrium and non-equilibrium segregation is provided by Paju and Grabke [70]. Phosphorus was found to segregate to austenite boundaries in an Fe-P alloy by the equilibrium segregation mechanism, the magnitude therefore decreasing with increasing austenitizing temperature. Some additional segregation took place on quenching from the austenitizing
Figure 2.13: Isothermal precipitation diagram for Laves phase in 9Cr-2Mo steels with varying silicon and manganese concentrations; CR(0.67Si, 0.58Mn), CA-1(0.008Si, 1.19Mn), CA-3(0.29Si, 1.24Mn), CA-4(0.66Si, 1.17Mn) [63].
temperature: non-equilibrium segregation. However, it was also found that the addition of manganese, to form an Fe-10Mn-P alloy, resulted in the segregation of phosphorus this time increasing with increasing austenitizing temperature. The manganese enhanced the diffusivity of phosphorus, hence increasing the non-equilibrium segregation during quenching; the increasing non-equilibrium segregation in this instance obscuring the decreasing equilibrium segregation.

Thus the as-tempered microchemistry of 12%Cr martensitic steels may exhibit remnants of non-equilibrium segregation together with equilibrium (co)segregation. Prolonged high temperature service will cause any non-equilibrium segregation to diffuse away but allow equilibrium segregation to approach equilibrium. It can also result in changes to the boundary microstructure, owing principally to the formation of Laves phase as boundary films.

### 2.2 Irradiation effects

#### 2.2.1 Defect generation

When materials are subjected to energetic particle irradiation (by electrons, ions or neutrons) lattice atoms may undergo elastic collisions with the incident particles. If the collision imparts a certain minimum energy, \( E_d \), to the lattice atom then it will be displaced from its lattice site, creating a self-interstitial and a vacancy: a Frenkel pair. The displaced atom is termed a primary knock-on atom (PKA), which itself is an energetic particle and consequently may displace further atoms.

Kinchin and Pease [71] developed the best known model for the subsequent interaction of the PKA with the lattice. Figure 2.14 plots the number of displaced atoms as a function of primary knock-on atom energy. At energies below the threshold energy, \( E_d \), no atomic displacement occurs. For energies between \( E_d \) and \( 2E_d \) the PKA can displace a lattice atom, but itself falls into the vacancy so created. At energies above \( 2E_d \) the PKA displaces one atom per \( 2E_d \) of energy, up to a cut-off energy, \( E_c \), above which the PKA loses energy not by elastic collision but by inelastic electronic excitation. The lower threshold energy, \( E_d \), depends not only on the particular material being irradiated, but also upon the crystallographic direction of displacement for any given material. Values of \( E_d \) range from 15 to 60 eV [72] with a value of 25 eV often taken as the average for iron [73]. This compares with typically 5 eV for the equilibrium thermal creation of self-interstitials; the difference arising from the highly irreversible nature of the displacement event [74]. The Kinchin-Pease model is highly simplified; in particular, taking no account of crystallographic effects, such as channelling, or of recombination effects, but it serves as a basis for understanding.
Figure 2.14: The number of displaced atoms in a displacement cascade as a function of primary knock-on atom energy as described by the Kinchin-Pease model [71].

Figure 2.15: Simulation of the point defect distribution in a displacement cascade; the primary knock-on atom enters from the lower left corner [75].

[\text{\text{-}} = \text{interstitial}, \text{\ast} = \text{vacancy}, \text{cube edge} = 125\ \text{atoms}.]
The sequence of displacement events resulting from the initial PKA is termed the displacement cascade. As the PKA slows down its mean free path decreases, leading to closer spaced intervals between displacements. As a result, the displacement cascade resembles a root-like structure as illustrated in Figure 2.15 [75]. One energetic PKA may displace several secondary knock-on atoms which in turn displace further atoms, until the energy of each of the displaced atoms falls below $E_d$. The cascade core is rich in vacancies, with interstitials being ejected to a surrounding shell. Theoretical modelling of the cascades done for absolute zero (0K) allows no thermal migration of point defects. This represents the nascent damage state, but the instantaneous thermal spike at the damage centre allows spontaneous athermal recombination of Frenkel pairs within a certain capture radius. Moreover, in the temperature range of interest for reactor operation, between 0.25 and 0.6$T_m$, both vacancies and self-interstitials are mobile. Hence mutual recombination of Frenkel pairs may occur after the collision event - at times greater than $10^{-12}$ sec - owing to elastic interaction. Point defects are also annihilated at fixed sinks such as surfaces, grain boundaries, dislocations and incoherent precipitate interfaces. The effective point defect concentration is further lowered by aggregation of defects to form vacancy platelets, which can act as void embryos, and interstitial clusters, forming embryonic dislocation loops. Figure 2.16 [76] demonstrates the variation of vacancy and interstitial concentration in irradiated nickel at a damage rate of $10^{-6}$ dpa s$^{-1}$ (typical of fast breeder reactor operation) as a function of temperature and sink density. It can be seen that irradiation dramatically increases the vacancy concentration above the thermal equilibrium concentration at temperatures below approximately 0.6$T_m$. The steady state irradiation generated interstitial concentration is several orders of magnitude less than the corresponding vacancy concentration, with a stronger dependence on sink density. For reference, in a thoroughly annealed alloy dislocation density is of the order of $10^{11}$ m$^{-2}$ and in a heavily cold worked or martensitic structure $10^{16}$ m$^{-2}$ [77].

Those vacancies and interstitials that escape the displacement cascade and are thus available as freely migrating defects constitute only a small proportion of those defects calculated as being generated by the cascade. The actual proportion of defects that are freely migrating is of great importance in quantifying and modelling defect flux driven irradiation effects such as void swelling, irradiation creep and radiation-induced segregation.

The production of freely migrating defects varies markedly with the irradiating species and energy, as reviewed by Rehn and Okamoto [78], but is thought to be independent of temperature [79,80]. The efficiency of generation of freely migrating defects is found to decrease significantly with increasing primary recoil energy, as illustrated in Figure 2.17 [78]. Irradiating species having high primary recoil energies are fast neutrons and heavy
Figure 2.16: (a) Vacancy and (b) interstitial concentrations in irradiated nickel as a function of temperature for a displacement damage rate of $10^6$ dpa s$^{-1}$.

(- - -) = sink density of $10^{12}$ m$^{-2}$, (-----) = sink density of $10^{15}$ m$^{-2}$, (-----) = thermal equilibrium concentration [76].
Figure 2.17: Relative efficiency of freely migrating defect production as a function of the average recoil energy of primary-knock-on atoms generated by irradiation [78].

Table 3

The fraction of freely migrating defects (FMD) produced in nickel by differing energies and species of irradiation [80].

<table>
<thead>
<tr>
<th>Irradiation species</th>
<th>FMD% (calc.)</th>
<th>FMD% (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MeV H⁺</td>
<td>8.8</td>
<td>20</td>
</tr>
<tr>
<td>2 MeV H⁺</td>
<td>7.1</td>
<td>9.6</td>
</tr>
<tr>
<td>2 MeV Li⁺</td>
<td>6.4</td>
<td>7.4</td>
</tr>
<tr>
<td>300 keV Ni⁺</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>3 MeV Ni⁺</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>3.25 MeV Kr⁺</td>
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<tr>
<td>200 keV O⁺</td>
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</tbody>
</table>
ions, which produce dense displacement cascades; electron and light ion irradiations give low primary recoil energies and little cascade damage, leading to a higher proportion of isolated Frenkel pairs. Irradiations with weighted average recoil energies of 74 keV are less than 2% as effective at generating freely migrating defects as those with weighted average recoil energies of 730 eV. Similarly Naundorf et al. [80] have compared their calculated values with experimental results for the fraction of freely migrating defects generated in nickel by different kinds and energies of ion irradiation. Their calculated values ranged from 1.2 to 8.8%; the experimental results from 0.4 to 20%, as given in Table 3. It can be seen that the fraction of freely migrating defects produced is not a straightforward function of irradiation species energy. For neutron irradiation, analysis by Kirk and Blewitt [81] implies that fast neutrons (with recoil energy of ~20 keV) are only a few percent as effective at producing migrating vacancies in Cu₃Au at 423K as thermal neutrons (recoil energy ~300 eV). Rehn and Okamoto [78] infer from published studies [82,83] of the Curie temperature of Ni-Si alloys that the freely migrating defect production during 14 MeV neutron irradiation (weighted average recoil energy 500 keV) is only 6-7% of that during 2 MeV electron irradiation (weighted average recoil energy 60 eV) at the same calculated dpa rate.

In summary, the direct consequence of exposure of a material to neutron (or other energetic particle) irradiation is to introduce an additional population of point defects into the lattice via displacement cascade events. The calculated point defect population consists of defects which may mutually annihilate, aggregate or become freely migrating. The displacement cascade spike plays an important role in the evolution of irradiated microstructure as reviewed by Averback and Seidman [84]. However, it is the non-equilibrium concentration of freely migrating defects which controls point defect flux driven mechanisms during irradiation. The efficiency of production of freely migrating defects by fast neutrons is not easily quantified but is of the order of only a few percent of the calculated point defect generation rate. Unfortunately this translates to a significant factor of uncertainty in the input parameter for modelling calculations.

2.2.2 Microchemical modification mechanisms

The effect that the primary damage, described above, has on the microstructure of a material in forming a secondary damage structure depends critically upon the material composition, initial microstructure and irradiation conditions. Compositional modifications within the microstructure may be induced by any of several mechanisms: preferential sputtering, displacement mixing, radiation-enhanced diffusion, radiation-induced segregation and Gibbsian adsorption (equilibrium segregation) [85]. A brief
review of the characteristics of these processes is presented below with radiation-induced segregation subsequently treated in more detail in Section 2.3.

### 2.2.2.1 Preferential sputtering

Preferential sputtering is a predominantly athermal surface effect. Displacement cascades are the physical origin of sputtering; when they occur in the vicinity of the surface they may impart sufficient energy to near-surface atoms and momentum in the outward direction to overcome their surface binding energy and be ejected. Two factors dictate that sputtering may be preferential. First, unequal atomic masses result in differing momentum transfers to atoms during atomic collisions. Second, each alloying element will have a particular surface binding energy and consequently will require a different kinetic energy to escape from the surface. The preferential loss of certain alloying elements from the surface layers results in a compositional variation of solute changing in spatial extent with time, until steady state is achieved when the sputtered-atom flux becomes equal to the bulk composition. This is shown schematically in Figure 2.18 [85]. Although preferential sputtering is predominantly athermal, its spatial extent is dependent upon the diffusional processes operating, such as Gibbsian adsorption and radiation-induced segregation, and hence will vary with temperature. Preferential sputtering effects have been extensively reviewed by Betz and Wehner [86].

### 2.2.2.2 Displacement mixing

Displacement mixing is also predominantly an athermal process arising from displacement cascades, but in contrast to preferential sputtering is a bulk rather than surface effect. A distinction can be made between two subdivisions of displacement mixing. Recoil implantation is the preferential transport of lighter atoms in the beam direction owing to greater momentum transfer. Cascade mixing is a random walk process being proportional to the site exchange frequency, $\nu$ [87-91]. This is related to the defect production rate, $K$ (displacements per atom per second, dpa s$^{-1}$), by $\nu = \psi K$ where $\psi$ is the total number of site replacements per dpa. Ion beam mixing and disordering experiments have shown that the number of atomic replacements per dpa in energetically dense cascades is of the order of 100 [84]. The displacement-induced diffusion coefficient may be written as:

$$D^*_k = \frac{<r^2> \psi K}{6}$$

where $<r^2>$ is the mean square jump distance. The site exchange frequency, $\psi K$, and thus the displacement-induced diffusion coefficient are assumed to be independent of temperature since the energies involved in the cascades are significantly greater than the
Figure 2.18: Schematic description of the preferential sputtering effect on the time evolution of the compositions of the sputtered-atom flux and of the near-surface region in a binary alloy A-B, where component A is sputtered preferentially [85].
thermal energies. Replacement collisions which occur during the collisional phase of the cascade (the first $10^{-12}$ sec) always randomize the lattice structure. However, events subsequent to this (at times greater than $10^{-12}$ sec) are affected by thermodynamic forces enhanced by the thermal spike at the damage centre and can lead to chemical mixing or ordering [92-95]. Fundamental aspects of displacement mixing have been reviewed by Averback [96].

### 2.2.2.3 Radiation-enhanced diffusion

The local atomic diffusion coefficients of A and B atoms in a binary alloy are proportional to the vacancy and interstitial concentrations, $C_v$ and $C_i$ respectively, and may be written as [97]:

\[
D_A = d_{Av} C_v + d_{Ai} C_i \\
D_B = d_{Bv} C_v + d_{Bi} C_i
\]

where $d_{Av}$ is the diffusivity coefficient for element A via vacancies, and so on. Therefore the irradiation enhancement of point defect concentrations will correspondingly enhance the atomic diffusion coefficients below temperatures of about $0.6T_m$. At temperatures above about $0.6T_m$, depending on irradiation-induced defect generation rate and sink density, the equilibrium concentration of vacancies exceeds that of radiation-induced defects (Figure 2.16) and so normal thermally activated diffusion via vacancy transport takes over. At low temperatures the supersaturation of irradiation generated vacancies is very high and vacancy mobility low, such that direct recombination with interstitials dominates over diffusion to fixed sinks. At intermediate temperatures most vacancies and interstitials will be lost by diffusion to fixed sinks, the proportion increasing with sink density.

The temperature dependence of the process and the effects of sink density and defect generation rate are illustrated in Figure 2.19 [98]. At faster defect generation rates the radiation enhancement of diffusion extends to higher temperatures (curve 1). For low sink densities the mutual recombination region extends directly to the regime of thermal equilibrium vacancy diffusion (curves 1 and 2). For higher sink densities mutual recombination gives way to annealing at fixed sinks at a critical temperature, above which the diffusion coefficient is independent of temperature until thermal equilibrium vacancy diffusion dominates (curves 3 and 4). Detailed reviews of the theories and measurement of radiation-enhanced diffusion are available [98,99].
Figure 2.19: The calculated self-diffusion rate of copper as a function of temperature for varying defect production rates, $K_o$, and dislocation densities, $\rho_d$. Curve 1: $K_o = 10^{-6}$ s$^{-1}$, $\rho_d = 10^{11}$ m$^{-2}$; Curve 2: $K_o = 10^{-6}$ s$^{-1}$, $\rho_d = 10^{14}$ m$^{-2}$; Curve 3: $K_o = 10^{-4}$ s$^{-1}$, $\rho_d = 10^{15}$ m$^{-2}$; Curve 4: $K_o = 10^{-4}$ s$^{-1}$, $\rho_d = 10^{17}$ m$^{-2}$ [98].
2.2.2.4 Radiation-induced segregation

The supersaturation of point defects during irradiation at temperatures below $0.6T_m$ that is responsible for radiation-enhanced diffusion is also the origin of radiation-induced segregation. This supersaturation is relieved at sinks, thereby causing point defect concentration gradients adjacent to the sinks. In consequence, point defect fluxes are generated. Since a point defect flux is always associated with a corresponding atomic flux, any solute participating preferentially in the defect exchange process or associating with a particular defect will result in the atomic flux differing from the local matrix composition. Spatial redistribution of alloying components will thus occur near to sinks: radiation-induced segregation. Radiation-induced segregation is a form of non-equilibrium segregation, but, unlike the non-equilibrium segregation generated by transient vacancy fluxes on cooling, steady state may be achieved during radiation-induced segregation since the defect fluxes to non-saturable sinks during irradiation are persistent. Several useful reviews of radiation-induced segregation have recently been published [100-102] and the mechanisms and experimental observations relating to 12% Cr steels are dealt with in detail in Section 2.3.

2.2.2.5 Equilibrium segregation

Equilibrium segregation has already been dealt with in Section 2.1.4.1, but the process can be modified by irradiation [85]. The matrix to interface jump frequency, $v_{A}^{m(L)}$, for $A$ atoms segregating from the matrix to the interfacial layer is given by:

$$ v_{A}^{m(L)} = v_{A}^{v}C_{v}^{m} + v_{A}^{i}C_{i}^{m} $$

where $v_{A}^{v}$ and $v_{A}^{i}$ are the jump frequencies for vacancies and interstitials with $A$ atoms and $C_{v}^{m}$ and $C_{i}^{m}$ are the matrix concentrations of vacancies and interstitials respectively. Irradiation therefore, by raising the point defect concentration, increases the matrix to surface jump frequency. Consequently the rate at which equilibrium segregation occurs is increased during irradiation at temperatures below about $0.6T_m$.

Of course, as well as occurring at grain boundaries equilibrium segregation occurs at free surfaces. As a result there will be an interaction between equilibrium segregation and preferential sputtering (Section 2.2.2.1). The time dependence of the evolution of near-surface composition is shown schematically in Figure 2.20 [85]. Since the surface composition is initially enriched in A atoms from equilibrium segregation, enhanced preferential sputtering of A atom occurs, as the sputtered flux is largely dependent upon surface layer composition. The concentration of A atoms in the adjacent layer reduces, in an attempt to regain the thermodynamic equilibrium segregated state. This continues until
Figure 2.20: Schematic description of the simultaneous effects of Gibbsian adsorption and preferential sputtering on the time evolution of the sputtered-atom flux composition and alloy composition in the near-surface region of a binary alloy A-B, in which component A is both adsorbed and sputtered preferentially [85].
steady state is reached when the sputtered-atom flux composition is equal to the bulk composition of the alloy.

2.3 Radiation-induced segregation

The origin of radiation-induced segregation has been outlined in Section 2.2.2.4 above. Descriptions of the process usually distinguish two mechanisms: that arising from tightly bound defect-solute complex migration and that from the inverse of the Kirkendall effect. Both mechanisms can, in principle, operate in conjunction with vacancies or interstitials. Defect-solute interactions and models of radiation-induced segregation based on them are discussed below, followed by a description of the inverse Kirkendall effect and its associated models. Finally an overview of the relative importance of each mechanism to radiation-induced segregation is given.

2.3.1 Defect-solute complexes

The formation of defect-solute complexes is easiest to visualize, and is conceptually most valid, in the case of a dilute alloy. Here each solute atom can be considered in isolation so that in general each point defect will have only one nearest neighbour solute atom. As described for non-equilibrium segregation (Section 2.1.4.2) there will normally be a binding energy between solute atoms and, in that case, vacancies. The binding energy is a result of the relaxation of some of the strain energy associated with both species as distinct entities when the two occupy nearest neighbour sites. In the case of irradiated materials there is not only a non-equilibrium concentration of vacancies, but of interstitials too, so that both vacancy-solute and interstitial-solute complexes may form.

2.3.1.1 Vacancy-solute complexes

The formation of a vacancy-solute complex is accomplished by bringing together an isolated vacancy and impurity to nearest neighbour sites. This is illustrated in Figure 2.21 [103] for the case of an oversized substitutional solute. The binding energy, $E_b$, for the vacancy-solute complex is the free energy difference of the lattice between the two states. Strain energy relaxation is obviously one factor in determining the binding energies - but so too are electronic and, in the case of $\alpha$-iron, magnetic effects [104].

Despite the importance of the vacancy-solute binding energy to atomistic processes in physical metallurgy, few reliable experimental values have been accumulated - even for single solute atom-monovacancy interactions. The experimental techniques used are based on measuring properties that are sensitive to the total vacancy concentration.
Figure 2.21: The formation of an impurity-vacancy pair by bringing together (a) an isolated oversized impurity and vacancy (b) to mutually relieve some of the strain energy associated with both species [103].

Figure 2.22: The relationship between the calculated vacancy-impurity binding energy, $E_b$, and impurity atom radius, $r$, in iron [109].
Measurement of the change in concentration when minor solute additions are present enables the vacancy-solute binding energy to be deduced from the apparent difference in vacancy formation energies for the pure metal and alloy. The techniques are often indirect and the complex results not always unambiguous. Most studies have been carried out using face-centred cubic crystals: in particular, aluminium, copper and gold. In general, the values for binding energies are low - most often -0.05-0.1 eV, and usually below 0.3 eV [100,105]. Larger values remain controversial [101].

Hautojarvi [106], in reviewing positron annihilation effects, ascribes the following properties of impurities in an $\alpha$-iron matrix to vacancy interaction.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Interaction with Vacancies</th>
<th>Stability Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>captures vacancies</td>
<td>vacancy-C pairs stable to 490K</td>
</tr>
<tr>
<td>Silicon</td>
<td>captures vacancies</td>
<td>pairs dissociate at 300K</td>
</tr>
<tr>
<td>Cobalt</td>
<td>only weak interaction</td>
<td>only weak interaction with vacancies</td>
</tr>
<tr>
<td>Manganese</td>
<td>weak interaction</td>
<td>weak interaction</td>
</tr>
<tr>
<td>Titanium</td>
<td>strong interaction</td>
<td>complexes stable to 550K</td>
</tr>
<tr>
<td>Antimony</td>
<td>strong interaction</td>
<td>complexes dissociate at 600K</td>
</tr>
</tbody>
</table>

Although the temperature at which the complex is stable to is an indication of the binding energy, as we shall see, the important criterion is whether the complex is able to migrate before it dissociates.

Because of its importance and difficulty in measurement, several attempts have been made to theoretically and empirically predict the vacancy-solute binding energy. These have been reviewed by several authors [100,105,107]. Early models calculated the electronic effects, representing a solute atom by a point charge or square well, and neglected relaxation effects. More recent models have been based on a pseudopotential method to determine interatomic potentials [108] and have also included relaxation effects [103]. However, successful application of pseudopotentials to a solid is limited to alkali and simple (i.e. non-transitional) metals. Attempts have also been made to apply macroscopic elastic theory on an atomic scale. In a recent approach Faulkner [109] has calculated impurity diffusion constants and vacancy-impurity binding energies, giving values for complexes in iron varying with solute radius as shown in Figure 2.22.

Two mechanisms for the motion of vacancy-solute complexes exist: caging and looping [110]. Vacancy-solute caging is the back and forth exchange between the solute atom and vacancy. Looping is the mechanism whereby the vacancy jumps between solute nearest neighbour sites. The combination of the two mechanisms permits long-range migration of the complex. The activation energy for the two mechanisms is that of vacancy
exchange with solute or solvent atoms respectively. Hence the migration energy, $E^{m}_{v}$, is often taken to be equal to the migration energy of the free vacancy, $E^{m}_{v}$.

2.3.1.2 Interstitial-solute complexes

It is well known that the presence of solute atoms interferes with the resistivity recovery of dilute alloys compared with pure metals [111]. The suppression of stages I_D and I_E in recovery experiments on irradiated materials is attributable to an interaction between the solute atoms and self-interstitials. This interaction can lead to the formation of stable interstitial-solute complexes. Their subsequent configurational changes and migration can cause distinct substages in stage II recovery. To understand the relative effect of different solutes on this interaction it is helpful to first consider the configuration and jump-modes of self-interstitials.

2.3.1.2.1 Self-interstitials

(i) Configuration

The configuration of self-interstitials in pure metals has been the subject of extensive discussion during conferences on point defects and is reviewed by several authors [112-115]. Again, most attention has been given to face centred cubic materials, although knowledge regarding body centred cubic and hexagonal materials in improving.

Lattice theory calculations, pioneered by Johnson [116,117], have calculated the most stable interstitial configurations for cubic crystals [114,118]. The configuration takes the form of a split-interstitial, or dumbbell. Two atoms are associated with a single lattice position. The two atoms have mutually repulsive cores and thus arrange themselves in the form of a dumbbell centred about the normal lattice site. The axis of the dumbbell has been found to be aligned in a (100) direction for face centred cubic metals and a (110) direction for body centred cubic metals, as shown in Figure 2.23 [114]. In order to accommodate the two dumbbell atoms the neighbouring atoms are displaced outwards, creating an elastic displacement field around the defect. This long range strain field results in self-interstitial formation energies being very high, approximately 4.5 eV for $\alpha$-iron [115], such that at thermal equilibrium their concentration can be regarded as negligible.

(ii) Jump processes

The jump process involved in the migration of the self-interstitial dumbbell in face centred cubic metals is found to be three dimensional, involving a translation with simultaneous rotation, as illustrated in Figure 2.24(a) [119]. One of the two dumbbell atoms moves
Figure 2.23: Stable self-interstitial configurations; (a) [100] dumbbell in the fcc lattice; (b) [110] dumbbell in the bcc lattice [112].

Figure 2.24: (a) Migrational jump of the [100] dumbbell in the fcc lattice with simultaneous reorientation. (b) Migrational jump of the [110] dumbbell in the bcc lattice with a simultaneous reorientation of 60°. (c) Migrational jump of the [110] dumbbell in the bcc lattice without reorientation (two dimensional migration) [119].
towards a nearest neighbour position, displacing the nearest neighbour to form a new
dumbbell with this partner, whilst the old partner returns to its original lattice point thus
allowing long range migration of the dumbbell.

The body centred cubic (110) dumbbell may undergo an analogous three dimensional
jump or a two dimensional jump, shown in Figures 2.24(b) and 2.24(c) respectively. In
the three dimensional jump there is a simultaneous translation in the original (110)
direction with a 60° rotation to form a new dumbbell lying on a different (110) axis.
Recent evidence for molybdenum [120] has shown that migration without reorientation
can also occur in body centred cubic metals. This two dimensional migration
 corresponds to a pure translation so that the dumbbell lies on a parallel axis after
migration. Johnson [121] has performed energy calculations and proposed a two step
process with an intermediary (223) split interstitial, Figure 2.25. The existence of this
two dimensional jump has been used by Evans [122] to explain planar ordering of voids in
molybdenum.

The activation energy for self-interstitial migration is low, ranging from only 0.01 eV for
Pb to 0.3 eV for α-iron [112,115] which is unusually high owing to magnetic effects [123].

2.3.1.2.2 Self-interstitial / solute interaction

Their large local lattice distortion and high elastic shear polarizability causes self-
interstitial dumbbells to interact strongly with other strain fields such as associated with
solute atoms, other self-interstitials and dislocations [113]. The interaction between self-
interstitials and solute atoms is dependent on the impurity size: whether it is over or
undersized with respect to the host lattice. In the vicinity of a solute atom there are a
number of possible configurations for the self interstitial dumbbell to adopt. Those
favoured will be where the displacement field of the solute atom fits best that of the self-
interstitial dumbbell. Configurations that are attractive for undersized impurities will be
repulsive for oversized, and vice versa.

Undersized impurity atoms are actually incorporated directly into the dumbbell, replacing
one of the host dumbbell atoms to form a mixed dumbbell configuration, illustrated in
Figure 2.26 [113]. The impurity atom is displaced toward the octahedral site, causing a
relaxation of the displaced lattice atoms towards their original sites as indicated by Figure
2.27 [114]. This relaxation in lattice distortion causes undersized solutes to form very
stable complexes with self-interstitial dumbbells. These complexes are stable to stage III
recovery with binding energies typically of 0.5-1.0 eV [113]; the binding energy, in
Figure 2.25: The migrational jumps for two dimensional interstitial migration in the bcc lattice, showing (b) the intermediary (223) dumbbell [121].
Figure 2.26: The mixed dumbbell configuration of an undersized impurity-interstitial complex in the fcc lattice, showing as dotted lines the axes of new mixed dumbbells which may be formed by motion of the impurity atom around the corners of the octahedral cage [113].

Figure 2.27: Structure of the mixed dumbbell for an undersized impurity atom in the fcc lattice, showing the relaxation of the atomic positions (●) towards the equilibrium positions (※) compared with the distorted positions of the self-interstitial (○) [114].
general, increasing with larger negative solute misfit, i.e. as the impurity atom size reduces.

Oversized impurities are not favoured to be incorporated into an interstitial dumbbell itself, since they would cause even greater lattice distortion. Thus they remain substitutional and instead trap self-interstitial dumbbells on nearest neighbour sites as illustrated in Figure 2.28 [114]. The trapping of self-interstitials is weaker for oversized impurities, with typical binding energies of 0.2-0.3 eV; the complexes in this case dissociating before stage III [113].

2.3.1.2.3 Complex migration

The important consequence of complexes in terms of radiation-induced segregation is not so much their formation, but their ability to undergo long range migration as a complex. Again, attention has been focused on the situation in face centred cubic metals - mechanisms in body centred cubic metals are more speculative. The mechanisms that have been put forward for complex migration in body centred metals [119] are analogies of the mechanisms for face centred materials, so it is helpful to deal with these first.

The equivalent jump to the self-interstitial jump (Figure 2.24(a)) is shown in Figure 2.29(a) [119]. It is apparent that in this case the mixed dumbbell is merely reoriented around the octahedral site: the solute atom stays in a cage centred on the octahedral site, the various configurations of which were shown in Figure 2.26. If instead the mixed dumbbell purely rotates, as in Figure 2.29(b), the solute atom is transferred to a different octahedral cage. Coupled with the previous cage motion (Figure 2.29(a)), long range migration of the solute-interstitial complex can occur. A further possibility, shown in Figure 2.29(c), is the jump of the host atom to form a self-interstitial dumbbell. The solute atom then returns to a substitutional site, thus the mixed dumbbell has dissociated and no long range migration of the solute atom occurs directly. If, however, the resultant self-interstitial dumbbell further jumps round in a loop back to the solute atom, as in Figure 2.29(d), the mixed dumbbell is reformed, but with the solute atom displaced to a different octahedral cage. Hence long range migration of the solute-interstitial complex is possible again.

For a self-interstitial trapped by an oversized solute atom only two jump modes are possible, shown in Figure 2.30 [119]. The first is a localized jump of the dumbbell around the twelve equivalent nearest neighbour sites (Figure 2.30(a)). Alternatively a dissociation jump may occur (Figure 2.30(b)). It is important to realize that in neither of these cases does solute atom transport occur.
Figure 2.28: The trapping configurations of a [100] dumbbell around an oversized impurity atom in the fcc lattice [114].
Figure 2.29: Possible diffusional jumps of the undersized impurity and host atoms incorporated in a [100] mixed dumbbell; (a) caging, (b) rotation, (c) dissociation and (d) looping [119].
Figure 2.30: Possible migrational jumps of a [100] self-interstitial dumbbell trapped by an oversized impurity; (a) reorientation, (b) dissociation [119].
Analogous motion of the (110) mixed dumbbell in the body centred system is possible. In this case there are only four equivalent sites on a plane around the octahedral centre that give rise to (110) mixed dumbbells, illustrated by Figure 2.31 [119]. Planar caging of the solute is possible (Figure 2.32(a)); as with the caging motion of the (100) mixed dumbbell (Figure 2.29(a)) no long range solute migration occurs so long as the solute atom remains in the same cage. A rotational jump with a 60° change of axis of the (110) mixed dumbbell is shown in Figure 2.32(b). Here the solute atom is transferred to a different planar cage; this jump combined with the caging motion thus leads to long range migration of solute atoms via an interstitial mechanism. Figure 2.32(c) shows a further possible jump: a combined translation and rotation related to the three dimensional jump of the self-interstitial dumbbell (Figure 2.24(b)). It also corresponds closely to the octahedral-octahedral diffusional jump of solute atoms in interstitial solid solution, such as carbon in α-iron. Finally, a two dimensional interstitial migration of solute atoms derived from the planar migration of self-interstitials (Figure 2.24(c)) has been proposed [124] and is illustrated in Figure 2.32(d). Besides these solute atom jump modes, dissociation of the mixed dumbbell to form a self-interstitial dumbbell configuration is possible, but this does not lead to long range solute migration.

The size effect model of Dederichs et al [114] predicts that for undersized solute mixed dumbbells, the activation energy for the caging motion is always lower than that for the migration of a self-interstitial dumbbell and than the rotation and dissociation energies of the mixed dumbbell. The rotation and dissociation energies increase with negative misfit whilst the caging energy decreases, Figure 2.33. From Figure 2.33 it can be seen that rotation and caging is favoured over dissociation of the mixed dumbbell for all but the least misfitting solutes. Robrock [119] argues that if it also holds for a (110) mixed dumbbell that the migrational potential is sinusoidal and that the activation energy scales with jump distance then one would expect planar caging to have the lowest activation energy, provided that the intracage jump distance is shorter than that of the intercage jump. Similarly, the direct jump of Figure 2.32(c) ought to be favoured over the 60° rotation (Figure 2.32(b)) and both over the one dimensional jump (Figure 2.32(d)).

2.3.1.3 Segregation from defect-solute complexes

From the preceding discussion it will be apparent that point defects can interact strongly with solute atoms to form solute-defect complexes. If the bound complexes are able to migrate in preference to dissociation then any point defect flux will incorporate a linked solute flux, leading to solute segregation at point defect sinks.
Figure 2.31: The planar cage of the [110] mixed dumbbell in the octahedral cell of the bcc lattice [119].

(a)

(b)

(c)

(d)

Figure 2.32: Possible jump modes of the [110] mixed dumbbell in the bcc lattice; (a) caging, (b) rotational jump, (c) octahedral-octahedral jump and (d) planar migration [119].
Figure 2.33: Ratio of the activation energy for the mixed dumbbell migration by various jump modes, $E_{md}$, to the migration energy of the [100] dumbbell, $E^m$, as a function of negative misfit of a solute atom, radius $r_o$, to the host atom, radius $R_o$ [114].
Rehn and Okamoto [101] give the criterion for complex migration:

\[ E_{m}^{d-s} < E_{b}^{d-s} + E_{m}^{d} \]

that is, when the migration energy of the defect-solute complex, \( E_{m}^{d-s} \), is less than the sum of the defect-solute binding energy, \( E_{b}^{d-s} \), and the defect migration energy, \( E_{m}^{d} \). Johnson and Lam [125] and Wiedersich et al [126] have calculated that defect-solute energies in excess of about 0.2 eV are required to produce significant segregation at temperatures in the range 300-600°C. As discussed previously, vacancy-solute binding energies are rarely greater than this, whereas undersized solute-interstitial complexes do have typical binding energies in excess of this. Oversized solute-interstitial binding energies are of the order of 0.2-0.3 eV but in their case the two possible migrational jumps do not lead to coupled solute migration.

Thus, strongly bound undersized solute-interstitial complexes are expected to play a dominant role in radiation-induced segregation via complex migration. In such cases undersized solutes will be enriched at point defect sinks.

### 2.3.1.4 Theoretical analysis

Johnson and Lam [125] were the first to develop a phenomenological model for radiation-induced segregation in dilute alloys, such that a point defect will usually interact with no more than one solute atom at a time: solute-defect complex formation can then be considered as an isolated pairwise interaction. The various complexes are continually forming and dissociating and the mobile defects diffuse in response to concentration gradients.

The Johnson-Lam analysis [125,127,128] considers six species: isolated vacancies, interstitials and solute atoms, vacancy-solute complexes and two types of interstitial-solute complex, one mobile and the other not. Ten basic reactions describe the irradiation, free interstitial-free vacancy recombination, formation and dissociation of complexes, interstitial-vacancy recombination via complexes and the sink interactions. Each reaction, and back reaction if any, is governed by its own rate constant. Six partial differential equations describe the rate of change in concentration of each species. Since analytical solution is not possible, these rate equations must be solved numerically, presenting formidable problems of stability and convergence. The rate equations are usually solved for a one-dimensional case, the coordinates being spherical for segregation to a void, cylindrical for segregation to a dislocation and cartesian for segregation to a planar surface.
The Argonne group have extended the Johnson-Lam approach in a proliferation of publications to include radiation-induced precipitation effects in undersaturated solid solutions [129,130] and the effect of depth dependent damage rates on solute redistribution in ion irradiated alloys [131]. The relationship between point defect trapping, solute segregation, radiation-induced precipitation and void growth has been investigated [126,132-134]. Subsurface compositional modifications during ion sputtering [135-139] compositional changes by non-uniform high voltage electron microscope irradiation [140-142] and solute redistribution processes in irradiated ternary alloys have also been modelled [143,144].

Following arguments by Allnatt et al [145] that Johnson and Lam's approach is not consistent with the kinetic theory of diffusion developed by Lidiard and co-workers (reviewed by Allnatt and Lidiard [146]) Murphy has developed a more rigorous model [74]. She has shown [147] that the Franklin and Lidiard [148] theory of diffusion in dilute alloys under thermal equilibrium may be extended to the case of an irradiated alloy. Johnson and Lam used geometrical arguments to obtain the rate equations: Murphy's model uses rigorously derived parameters for the interaction between solute and point defects in terms of the various jump frequencies of the vacancies and interstitials. Numerical integration is again necessary to solve the set of coupled rate equations.

An innovative approach to modelling radiation-induced segregation in dilute alloys via interstitial-solute complex migration has recently been proposed by Faulkner et al [149]. The approach is based upon non-equilibrium segregation theory, but assumes that solute transport to (or from) boundaries is exclusively via coupling to the interstitial flux, by the formation and migration of solute-interstitial mixed dumbbell complexes. For undersized solutes, where the binding energy to self-interstitials is much greater than to vacancies, this assumption may be justified. The approach does not require the numerical solution of coupled partial differential equations, as rate theory does, but does depend critically, as indeed all the approaches do, upon accurate enthalpies of binding and migration for the interstitial-solute complexes being known. The model treats solutes individually with no regard for synergistic or competitive effects, which may become relatively more important at lower dose rates and higher temperatures where the point defect supersaturation becomes less. However, the model is thought to accurately predict the relative magnitude of segregation and its variation with temperature, dose rate and sink strength.

The model of Faulkner et al [149] has been used to predict specific results for radiation-induced segregation of individual solutes in ferritic iron, illustrating also the general trends of the process. Figure 2.34 [150] shows the predicted temperature variation for
Figure 2.34: Model predictions of the radiation-induced segregation of silicon in α-iron as a function of irradiation temperature [150].

Figure 2.35: Model predictions of the radiation-induced segregation of phosphorus in α-iron as a function of irradiation temperature [150].
Figure 2.36: Model predictions of the radiation-induced segregation of nickel in α-iron as a function of irradiation temperature at varying damage rates to a total damage level of 1 dpa [149].
radiation-induced segregation of silicon in ferritic iron at a dose rate typical of fast reactor operation, and Figure 2.35 the corresponding predicted variation for phosphorus. Maximum segregation is predicted to occur at intermediate temperatures. At low temperatures the point defect supersaturations are very large and vacancies relatively immobile. Thus, at steady-state, most interstitials are annihilated by recombination with vacancies, rather than by long range diffusion to sinks, and hence relatively little solute segregation occurs. At high temperatures the increased thermal vacancy emission decreases the vacancy concentration gradients adjacent to sinks. In addition, back diffusion of the segregant down its own concentration gradient is increased by thermal activation, making concentration profiles across an interface shallower and wider than at the peak in radiation-induced segregation at intermediate temperatures. Raising the damage rate shifts this peak to higher temperatures, as shown in Figure 2.36 [149] for the predicted radiation-induced segregation of nickel in ferritic iron. At greater damage rates the thermal population of vacancies does not become equal to the concentration generated by irradiation until higher temperatures.

2.3.2 Inverse Kirkendall effects

2.3.2.1 Kirkendall effect

From a now classic set of experiments, Smilgalskas and Kirkendall [151] showed that a gradient in alloy composition can induce diffusion of a net flux of point defects across a 'marker' plane, thereby causing motion of the plane. The so-called Kirkendall effect occurs if an inhomogeneous alloy whose constituents have differing diffusivities is annealed. There will be a greater flux of the faster moving species in one direction than that of the slower moving species in the other. The net difference between the atomic fluxes is balanced by a flux of point defects. It is well established that thermal diffusion occurs via vacancy exchange and hence it is a vacancy point defect flux that occurs during the Kirkendall effect.

2.3.2.2 Inverse Kirkendall effect

Anthony [152] first argued, by analogy to his observations of solute redistribution in a vacancy flux, that an initially homogeneous alloy under irradiation could develop regions where the composition significantly differs from the initial value. Marwick [153] and Wiedersich et al [154] developed the theory in which the inverse of the Kirkendall effect occurs, whereby now a point defect concentration gradient induces net diffusion of atomic species. The defect fluxes generated during irradiation are naturally associated with atomic fluxes. Faster diffusing species will exchange more quickly with the point defect flux, thereby causing the composition of the atomic flux to differ from that of the
Figure 2.37: Schematic representation of the inverse Kirkendall effect induced near to a defect sink by a vacancy flux, $J_v$, in a binary alloy A-B [101].

Figure 2.38: Schematic representation of the inverse Kirkendall effect induced near to a defect sink by an interstitial flux, $J_i$, in a binary alloy A-B [101].
bulk. In contrast to the purely vacancy driven Kirkendall effect, the inverse Kirkendall effect may in principle be induced by both vacancy and interstitial fluxes generated by irradiation.

Graphical descriptions of the inverse Kirkendall effect induced by a vacancy and an interstitial flux are given by Rehn and Okamoto [101]. A representation of a vacancy concentration gradient near a defect sink in a binary alloy A-B inducing an inverse Kirkendall effect is shown in Figure 2.37. The vacancy gradient generates a vacancy flux, $J_v$, toward the defect sink, requiring a balancing atomic flux $(J_A^V + J_B^V)$ in the opposite direction, where $J_A^V$ and $J_B^V$ are the vacancy exchange fluxes of atomic species A and B respectively. These atomic fluxes will be in direct proportion to their local atomic fractions, $C_A$ and $C_B$ and to their partial diffusion coefficients, $D_A^V$ and $D_B^V$, such that:

$$\frac{J_A^V}{J_B^V} = \frac{D_A^V C_A}{D_B^V C_B}$$

Thus, when $D_A^V$ differs from $D_B^V$ the flux of the faster diffusing species will be proportionately greater than that of the slower. Hence the vacancy-induced inverse Kirkendall effect will cause the faster diffusing species to be depleted at a sink, and therefore cause enrichment of the slower diffusing species.

The situation for an inverse Kirkendall effect induced by an interstitial concentration gradient is shown schematically in Figure 2.38. Here, the interstitial flux, $J_I$, and the associated atomic flux $(J_A^I + J_B^I)$ flow in the same direction. Consequently, any difference in the partial diffusion coefficients of A and B atoms via interstitials, $D_A^I$ and $D_B^I$, will result in preferential transport of the faster diffusing species in this case towards the sink.

It can thus be seen that the inverse Kirkendall effects for the faster diffusing alloy component generated by both species of point defect flux are in opposite directions. The net result depends on the relative magnitudes of the ratios $D_A^V / D_B^V$ and $D_A^I / D_B^I$, such that the atomic transport driven by each defect species may be in concert or opposition.

2.3.2.3 Theoretical treatment

For concentrated alloys, treatment of the solute as isolated atoms is no longer valid: in this case, each vacancy, interstitial or lattice atom has approximately the same surroundings as all others of its species. Most approaches follow the random alloy theory for the motion of vacancies and solute atoms at thermal equilibrium of Manning.
This considers the motion of one solute atom through an homogeneous medium represented by the mean properties of the alloy. The jump frequencies of atom-vacancy exchange are characteristic of the atom species involved and alloy composition.

Marwick [153] derived a model for the flux of one species of a binary alloy as a result of the imposition of a vacancy gradient. He noted that for the case of an irradiated alloy the effect of the irradiation generated population of interstitials must be included, but then neglected it by assuming that the interstitial flux was neutral. In other words, the local flux of interstitial atoms was taken to contain A and B atoms in the same proportion as the local alloy compositions:

$$\frac{J_A}{J_B} = \frac{C_A}{C_B}$$

The flux of A atoms (assumed to be the faster diffusing species) up the vacancy gradient was calculated to be proportional to the difference in tracer diffusion coefficients of the two species:

$$ΩJ_A = -(D_A C_B + D_B C_A) \nabla C_A + C_A C_B \nabla (D_A^* - D_B^*)$$

where $D_A, D_B$ are the intrinsic diffusion coefficients of A and B.

$D_A^*, D_B^*$ are the tracer diffusion coefficients.

Wiedersich et al [154] extended the analysis to take into account the preferential migration of irradiation-induced interstitials also leading to solute segregation. They derived the following relationship between the steady state concentration gradient of component A and the vacancy concentration gradient:

$$\nabla C_A = \frac{D_A^* D_A^b}{\alpha (D_A^b D_A^* + D_B^b D_B^*)} \left( \frac{D_B^*}{D_B^b} - \frac{D_A^*}{D_A^b} \right) \nabla C_V$$

where $D_A^*, D_B^*$ are the partial diffusion coefficients of an interstitial diffusing via A and B atom exchanges; $D_A^{IRR}, D_B^{IRR}$ are the total radiation-enhanced diffusion coefficients for the A and B atoms; $\alpha$ is a thermodynamic factor to account for non-ideal solutions. Since the vacancy concentration gradient is always negative near a sink this relationship predicts an enrichment of A atoms at the sink when the preferential transport of A atoms via interstitials is greater than that by vacancies, i.e. when:

$$\frac{D_A^*}{D_B^*} > \frac{D_A^b}{D_B^b}$$
The relationship reduces to that of Marwick when $D_1' = D_2'$.

Further developments have been made by Perks et al [156] and Perks and Murphy [157] by the inclusion of the correlation and thermodynamic factors for diffusion. Thermodynamic factors arise because the free energy of the system depends on the arrangement of atoms - for instance, clustering of like atoms may reduce the free energy. Inclusion of these factors reduced the predicted segregation, but did not alter the shape of the profile. Temperature dependent values of the thermodynamic factors are poorly known and so the factors were actually set to zero when generating results from their analysis. Results of their calculations for radiation-induced segregation in an austenitic Fe-20Cr-25Ni alloy illustrating the effects of irradiation conditions are summarized below.

Figure 2.39 shows predicted segregation profiles of the three constituents indicating substantial solute redistribution within 10 nm of the boundary. Nickel, the fastest diffusing species, is enriched; chromium, the slowest, is depleted. The dose dependence of the magnitude of segregation is shown in Figure 2.40: steady state is eventually reached when the flux of segregant back-diffusing equals the radiation-induced flux. The predicted peak in segregation at intermediate temperatures is indicated in Figure 2.41. At low temperatures the greater point defect supersaturation and relative immobility of vacancies leads to a high proportion of defects annihilating by recombination rather than long range diffusion to sinks. At high temperatures the thermal emission of vacancies is comparable to the irradiation generated vacancy concentration, thereby reducing concentration gradients at sinks, whilst thermal activation also increases the rate of back diffusion. The actual profiles become wider and shallower with increasing irradiation temperature (Figure 2.42) and decreasing damage rate (Figure 2.43), since both act to reduce the point defect supersaturation.

2.3.3 Overview of mechanisms and models

It is convenient, if perhaps artificial, to separate radiation-induced segregation into the two distinct mechanisms of bound solute-defect complex migration and the inverse Kirkendall effect as being relevant to dilute and concentrated alloys respectively. It is likely that the two mechanisms will be acting, with either interstitials or vacancies or both, simultaneously.

The concept of tightly bound solute-defect pairs is valid only for solute concentrations of less than about 1 at.%, since the point defect in question must have only one solute atom as a nearest neighbour. If, as at higher concentrations, the defect had more than one
Figure 2.39: Predicted segregation profiles in an Fe-20Cr-25Ni alloy following 450°C irradiation at a damage rate of $2 \times 10^8$ dpa/s to 1 dpa [157].

Figure 2.40: The dose dependence of chromium segregation in an Fe-20Cr-25Ni alloy following 450°C irradiation at a damage rate of $2 \times 10^4$ dpa/s [157].
Figure 2.41 : The predicted variation in boundary plane concentration with temperature in an Fe-20Cr-25Ni alloy following irradiation to a damage level of 1 dpa at a damage rate of $2 \times 10^{-8}$ dpa/s [157].
Figure 2.42: The predicted effect of temperature on the chromium distribution in an Fe-20Cr-25Ni alloy following irradiation to a damage level of 1 dpa at a damage rate of $2 \times 10^{-8}$ dpa/s [157].

Figure 2.43: The predicted effect of damage rate on the chromium distribution in an Fe-20Cr-25Ni alloy following 450°C irradiation to a damage level of 1 dpa [157].
solute atom in its immediate environment, the defect may jump from one to the next, continually reforming solute-defect complexes as it does. The solute-defect complex would thus 'migrate', but without a corresponding solute flux.

Defect-solute interaction also becomes less effective as the temperature increases; hence inverse Kirkendall effects may dominate at higher temperatures. If both mechanisms are interstitial-driven, no change in the sense of segregation will occur. If, however, vacancies are the dominant point defect responsible, there may be a reversal of segregation direction at some temperature. Discounting interstitial effects, Wiedersich et al [126] have calculated that for dilute nickel binary alloys the segregation sense will change with temperature if the vacancy-solute binding energy is in the range 0.1-0.2 eV. For lower binding energies than this the inverse Kirkendall effect will dominate, causing solute depletion; for higher binding energies segregation is dominated by vacancy-solute complex diffusion, leading to solute enrichment.

Rehn and Okamoto in their review [101] came to the conclusion from available experimental results for dilute binary nickel alloys that a simple size effect rule, whereby undersized solutes are enriched and oversized depleted, rather than thermal diffusion data was the better predictor of radiation-induced solute segregation. This indicates that interstitial-solute complex migration dominates radiation-induced segregation. Rationalization of this comes from the trapping and migration mechanisms reviewed earlier. Undersized solute-interstitial complexes generally have higher binding energies than those formed with oversized solutes - reflecting a fundamental difference in their trapping configuration. Undersized solutes are incorporated directly into the self-interstitial to form a mixed dumbbell. The migration energy of these complexes is predicted to be less than their dissociation energy and therefore the undersized solute-interstitial complex migrates as a distinct species. Oversized solutes are also effective at trapping interstitials. However, as discussed previously, with sufficient thermal energy the complexes dissociate rather than migrate. Consequently, a self-interstitial flux passes by oversized solutes, leaving them substitutional. This net transfer of solvent atoms to defect sinks causes the observed relative depletion of oversized solute atoms.

Radiation-induced segregation in ternary alloys (and other more complex alloys) is not straightforward. For instance, in binary nickel alloys silicon (undersized) is enriched and aluminium (oversized) depleted at boundaries during irradiation. It might be expected from the size effect rule that in a nickel-silicon-aluminium ternary alloy that again silicon will become enriched and aluminium depleted during irradiation. This was not found to be the case [158]. The boundary regions were found to be enriched in silicon, but the aluminium/nickel ratio was found instead to be constant across the boundary plane. The
explanation given for this was that the observed enrichments and depletion in the binary alloys were caused by the same species of point defect flux, i.e. an interstitial flux. In the ternary alloy, the presence of a sufficient quantity of the undersized silicon atoms preferentially traps interstitials, thereby forming complexes which migrate to sinks. The interstitial flux is thus ineffective in transporting solvent nickel atoms via an interstitialcy mechanism in preference to aluminium atoms.

The models developed for radiation-induced segregation in dilute binary alloys give reasonably good agreement with experimentally determined concentration profiles. However, these models do require a large number of poorly known parameters such as the interstitial and vacancy jump frequency in the vicinity of solutes and reaction rate constants. Additionally, the solute concentration is generally limited to very low levels for the approximation of a dilute alloy to remain valid. This is particularly true for systems where solute enrichment is expected, since near to point defect sinks the large increases in concentration will invalidate the assumption if the initial concentration is not sufficiently dilute.

The models for concentrated alloys are less sophisticated than for dilute alloys, including possibly unrealistic assumptions concerning interstitial behaviour. The situation in concentrated alloys is actually more complex than in dilute alloys because of additional thermodynamic factors such as those concerning solute clustering.

Real engineering materials are, of course, invariably multicomponent alloys, usually containing both dilute and concentrated solute additions, which theoretical modelling is, as yet, unable to deal with. Even minor solute additions can strongly influence the segregation behaviour of the other solutes. Furthermore, most of the modelling has focused on face centred cubic materials: model alloys such as dilute nickel binaries or iron-chromium-nickel ternary alloys to approximate austenitic stainless steels. To investigate radiation-induced segregation effects in technological ferritic steels it is therefore necessary to actually experimentally determine solute concentration profiles at sinks in irradiated material.

2.4 Experimental observations of RIS in ferritic alloys

Experimental observations of radiation-induced segregation in ferritic alloys have been few, with most published work produced by the groups at Hokkaido University, Japan and Battelle Pacific Northwest Laboratories, USA. Most studies have been performed by accelerated testing, using either electron or ion irradiation. Analytically, Auger electron spectroscopy (AES) or energy dispersive X-ray microanalysis (EDX) by scanning
transmission electron microscopy (STEM) have been used to determine segregation profiles. The particular merits of these techniques will be discussed after a resume of experimental results.

2.4.1 Results

Turning to the Japanese group, their first results came from ion irradiated Fe-13%Cr, Fe-13%Cr-1%Ti and Fe-13%Cr-1%Si, Ohnuki et al [159]. The irradiation was performed with 200 keV C+ ions at 525°C to a maximum dose of 118 dpa at a rate of 8 \times 10^{-3} \text{ dpa/s}. Analysis was carried out by STEM-based EDX, the results of which are shown in Figure 2.44. When present as the only solute or in the presence of silicon, chromium was found to be strongly enriched at grain boundaries. The addition of titanium was found to cause slight grain boundary depletion of chromium, with the titanium itself being strongly enriched at the boundary region. These results can be attributed to the formation of grain boundary carbides brought about by implanting the specimens with carbon during irradiation which migrates and forms grain boundary precipitates with the stronger carbide forming element. Thus the results are not particularly useful in determining radiation-induced segregation effects.

Takahashi et al [160] studied solute segregation to grain boundaries in Fe-5%Cr, Fe-13%Cr and Fe-1%Mn alloys. In situ irradiation was performed in a high voltage electron microscope (HVEM) using 650 keV electrons to give a total damage level of 3 dpa at a rate of 5 \times 10^{-4} \text{ dpa/s} at 400°C. EDX was used to determine concentration profiles, examples of which are given in Figure 2.45. Wide zones of solute depletion about grain boundaries were observed for all three alloys.

The same authors [161] have also investigated grain boundary segregation in an irradiated Fe-1%Ni alloy. Electrons of energy 1 MeV generated damage at a rate of 2 \times 10^{-3} \text{ dpa/s} to 20 dpa at 400°C. EDX analysis across grain boundaries revealed an increase in nickel concentration on the boundary, where nickel rich precipitates were observed to form. Such precipitates were also observed at dislocation loops.

The group has published [162] results of radiation-induced segregation in an Fe-0.5%P alloy irradiated by 1 MeV electrons to a total dose of up to 15 dpa at 2 \times 10^{-3} \text{ dpa/s} in the temperature range 350 to 510°C. Compositional analysis by EDX revealed a slight depletion in the boundary concentration of phosphorus relative to the matrix after irradiation at all irradiation temperatures. The depletion was found to become more pronounced at increasing total damage levels and was greatest at the intermediate irradiation temperature of 470°C. This reduction in phosphorus concentration was
Figure 2.44: Solute concentration profiles after irradiation with 200 keV C⁺ ions to a damage level of 57 dpa at 525°C in: (a) Fe-13Cr, (b) Fe-13Cr-1Si and (c) Fe-13Cr-1Ti [159].
Figure 2.45: Solute concentration profiles in electron irradiated (a) Fe-5Cr and Fe-13Cr alloys, and (b) an Fe-1Mn alloy [160].
attributed to segregation and enhanced grain boundary diffusion of the solute to the foil surfaces where it could be lost.

The most recently published work of the group [163] concerns radiation-induced segregation in ternary ferritic Fe-Cr-Mn alloys: Fe-10Cr-3Mn, Fe-5Cr-5Mn and Fe-3Cr-7Mn being the compositions investigated. Again the irradiations were performed in an HVEM using 1 MeV electrons to a total dose equivalent of 15 dpa at $4 \times 10^{-3}$ dpa/s, the irradiation temperatures being 450, 500 and 550°C. Figure 2.46 shows the results of EDX analyses across grain boundaries of the irradiated materials. In the high chromium alloy depletion of chromium at the grain boundaries was found after irradiation at 450 and 500°C, but little variation in manganese concentration was detected (Figure 2.46(a)). In the high manganese alloy, substantial increases in manganese concentration were seen at each irradiation temperature, extending to 1 μm either side of the boundary (Figure 2.46(c)). A slight increase in boundary concentration was observed at the highest irradiation temperature; 550°C. Segregation of both solutes to boundaries was found in the Fe-5Cr-5Mn alloy (Figure 2.46(b)), the segregation increasing with irradiation temperature.

The group have also investigated radiation-induced segregation to dislocation loops in Fe-10Cr, Fe-10Cr-0.03C, Fe-1Ni and Fe-1.8Mo alloys [164]. The temperature range of 1 MeV HVEM irradiation was 290-500°C. Chromium enrichment at a(100) dislocation loops was seen; the enrichment being greater in the carbon containing alloy. The effect was hence attributed to the precipitation of chromium-rich carbides. Nickel-rich γ phase formed at dislocation loops in the binary iron-nickel alloy. The precipitates dissolved during post-irradiation annealing; implying that the phase is radiation induced. The authors reported molybdenum depletion at voids in the same work.

Finally, in collaborative work with the Batelle Pacific Northwest Laboratory, Takahashi et al [165] investigated solute segregation in two Fe-2.4Cr alloys with additions of 0.5 and 1.0% vanadium. The alloys were irradiated by 1 MeV electrons to 1.2 dpa at 400°C and a dose rate of $2 \times 10^{-2}$ dpa/s. Spatial compositional variation at grain boundaries and dislocation loops was determined by EDX. Chromium enrichment was detected at grain boundaries, whilst vanadium and chromium were found to be enriched at dislocation loops.

The Batelle group have principally used ion irradiation and AES in their studies of radiation-induced segregation. Brimhall et al [166,167] investigated surface segregation in HT-9, a commercial grade 12CrMoVW steel (see Table 1). Irradiation to a dose of 2 dpa at a rate of $3 \times 10^{-3}$ dpa/s was performed using 5 MeV Ni²⁺ ions at temperatures of 400 to
Figure 2.46: Segregation profiles across boundaries in three Fe-Cr-Mn alloys, (a) Fe-10Cr-3Mn (b) Fe-5Cr-5Mn (c) Fe-3Cr-7Mn, electron irradiated at three temperatures, (i) 723 K (ii) 773 K (iii) 823 K, to 15 dpa [163].
700°C. No significant subsurface redistribution of major or minor alloying elements was detected by AES; the only observed effect being a slight increase in the surface concentration of nitrogen after irradiation.

In a later study the same authors [168] examined surface segregation in HT-9 and two binary iron-phosphorus alloys containing 0.33 at.% and 0.1 at.% phosphorus. Nickel ion irradiation was again used to generate damage levels ranging from 0.01 to 12 dpa at temperatures from 400 to 600°C. Slight surface enrichment of phosphorus was detected in HT-9 after irradiations up to 0.8 dpa, with similar results obtained for irradiations of the binary iron-phosphorus alloys. However, no phosphorus segregation was detected at doses greater than 3 dpa and no measurable radiation-induced segregation of the other alloying elements in HT-9 such as chromium, nickel or molybdenum could be discerned.

Ion irradiation causes the sputtering of a specimen's surface layers as described in Section 2.2.2.1. Since ion irradiation causes damage only in a narrow region to shallow depths, all the phosphorus from the damage region could have accumulated at the surface by the time the received dose is 1 dpa. Doses in excess of this could remove segregated surface layers without the possibility of replenishment. Thus any segregant may be sputtered away during irradiation to high damage levels.

In more recent collaborative work [169] the group carried out one of only the three reported examinations of radiation-induced segregation in neutron irradiated ferritic materials. The reduced activation alloys Fe-9Cr-1W-2Mn and Fe-12Cr-1W-6Mn were neutron irradiated in the Fast Flux Test Facility / Materials Open Test Assembly (FFTF/MOTA) to a nominal dose of 10 dpa at 365°C. Specimens were fractured and their fracture surfaces analysed in situ by AES. Significantly increased concentrations of silicon and manganese were found on the fracture facets of the irradiated 9Cr and 12Cr steels respectively. No significant effect of irradiation on the segregation behaviour of phosphorus or sulphur could be detected - despite the fracture mode changing from transgranular to intergranular following irradiation.

Clausing et al [170] also examined neutron irradiated material. HT-9 martensitic steel specimens were irradiated in the Experimental Breeder Reactor II (EBR II) at 410, 520 and 565°C to a damage level of 13 dpa. Analysis was carried out by AES after in situ fracture of the irradiated specimens. The composition of large smooth facets on the fracture surface, thought to be prior austenite grain boundaries, was considerably enhanced in chromium, nickel, silicon and phosphorus compared to the bulk composition after neutron irradiation at 410°C, as shown in Figure 2.47. Such facets were not present on the fracture surface of specimen irradiated at 520 or 565°C, nor the thermal controls.
Figure 2.47: Compositional depth profiles from fracture facets in HT-9 which had been neutron irradiated in EBR-II at 410°C to a damage level of 13 dpa [170].
Kameda and Bevolo [175] attempted to produce radiation-induced segregation effects by neutron irradiation in a series of iron alloys doped with approximately 0.04%P, 0.005%S and 0.001 to 0.01%C. The specimens were neutron irradiated at the Los Alamos Meson Physics Facility A-6 target station to a dose of about 0.005 dpa at only 130°C. Since little radiation-induced segregation is expected at this temperature the specimens were subsequently aged at 450°C for 1 hour in an attempt to generate point defect fluxes to sinks by relieving the frozen-in point defect supersaturation. Specimens were then fractured and analysed in situ by AES. No discernible difference in segregation of phosphorus or sulphur to intergranular fracture surfaces could be detected after this neutron irradiation and ageing treatment.

Recently Muroga et al [172] used 1.0 and 1.25 MeV electron irradiation at a rate of 4.8 x 10^-4 dpa/s to 3.1 dpa at 500 and 600°C to investigate radiation-induced segregation in a commercial grade martensitic steel, JFMS (see Table 1), and high purity Fe-10Cr, Fe-10Cr-1Ni and Fe-10Cr-5Ni model alloys. Spatial variation in composition at grain boundaries, precipitate-matrix interfaces and dislocation loops was analysed by EDX. Chromium was found to be depleted at grain boundaries and precipitate-matrix interfaces in all alloys. Silicon enrichment at grain boundaries and precipitate-matrix interfaces in the JFMS was detected after irradiation. The segregation of nickel was found to depend upon the sink type. At the interstitially biased a (100) dislocation loops nickel enrichment took place; at grain boundaries slight depletion and at MC precipitate-matrix interfaces significant depletion occurred, thus implying competitive mechanisms for nickel segregation.

More recently still, Jung and Klein [173] have reported radiation-induced segregation in DIN 1.4914 martensitic stainless steel (the German equivalent of the FV448 used in this work, see Table 1) after 6.3 MeV proton irradiation to 0.06 and 0.64 dpa at 520°C. They analysed the variation in composition across large M_23C_6 and NbC precipitates to infer radiation-induced segregation: their analytical technique did not allow them to generate compositional profiles across grain boundaries. Silicon was found to be enriched at M_23C_6 interfaces with phosphorus, significantly, and silicon and manganese, slightly, enriched at NbC precipitate interfaces.

Finally, the most extensive study of radiation-induced segregation in ferritic materials has been performed by Mahon [174,175]. He studied a range of model ferritic alloys with a base composition Fe-12Cr-0.5Ni-0.5Mn. One alloy had simply the base composition, others were made having additions of 400 ppm phosphorus, 1% silicon, 2% vanadium, 2% molybdenum and 1% silicon with 2% molybdenum respectively. Specimens were
analysed by STEM-based EDX after irradiating with either 52 MeV Cr\textsuperscript{2+} ions to 10 dpa at a rate of 2.7 x 10\textsuperscript{-4} dpa/s at 550°C or 1 MeV electrons to 10 dpa at a rate of 2.7 x 10\textsuperscript{-3} dpa/s in the range 350 to 650°C. His specimens were fully ferritic and essentially dislocation-free prior to irradiation. Results from the base alloy showed grain boundary depletion of chromium and enrichment of nickel at all temperatures. Peak segregation was observed after electron irradiation at 550°C, the segregation profiles becoming wider and less steep with increasing temperature as more back diffusion becomes possible. Comparing ion and electron irradiations of the base alloy to the same total dose at a temperature of 550°C he found greater segregation in the electron irradiated alloy. Results from the alloys with additional solutes revealed depletion of molybdenum and vanadium, together with chromium, and enrichment of silicon and phosphorus along with nickel. The minor solute additions had no measurable effect on the segregation of chromium during irradiation. The addition of silicon to the base alloy greatly enhanced the segregation of nickel to the grain boundaries. Extensive grain boundary precipitation of M\textsubscript{23}C\textsubscript{6} in all alloys containing vanadium or molybdenum was detected after ion irradiation but not after electron irradiation. Only in the presence of both molybdenum and silicon did boundary precipitation occur during electron irradiation.

2.4.2 Summary

The results of the various studies of radiation-induced segregation in ferritic steels described above are summarized in Table 4. It can be seen that the results are not entirely consistent for the direction of segregation of individual solutes.

In the absence of precipitation, chromium is seen to be depleted from defect sinks in binary and ternary alloys. The segregation of chromium in commercial grade 12%Cr steels is less clear. The studies of Brimhall \textit{et al} [166-168], Jung and Klein [173] and Kimura \textit{et al} [169] reported no segregation effects for chromium. Muroga \textit{et al} [172] observed chromium depletion as did Mahon [174] in his very low carbon model 12%Cr alloys in the absence of precipitation effects. Clausing \textit{et al} [170], however, detected chromium enrichment in their AES analysis. As discussed later, this apparent increase in boundary concentration may be caused by the inclusion of chromium-rich boundary precipitates in the Auger analysis.

Nickel was always observed to be enriched at sinks in binary and ternary ferritic alloys. In the case of commercial grade 12%Cr steels Jung and Klein [173] and Brimhall \textit{et al} [166-168] reported no nickel segregation (although the use of nickel ion irradiation in Brimhall's studies would make interpretation difficult). Clausing \textit{et al} [170] detected nickel enrichment to a depth far greater than the profile widths for the other elements.
Table 4

Observations of radiation-induced segregation studies in irradiated ferritic materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Irradiation</th>
<th>Method of analysis</th>
<th>Observations of Segregation</th>
<th>Reference</th>
</tr>
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<tr>
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<td>Dose (dpa)</td>
<td>Temperature (°C)</td>
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<td>Fe-1Ni</td>
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<td>350 - 510</td>
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<td>5 MeV Ni²⁺</td>
<td>3 x 10⁻³</td>
<td>2</td>
<td>400 - 700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-0.03P</td>
<td>5 MeV Ni²⁺</td>
<td>1.5 x 10⁻³</td>
<td>2</td>
<td>400 - 700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-0.33P</td>
<td>Fe-0.1P</td>
<td>5 MeV Ni²⁺</td>
<td>NR</td>
<td>0.01-12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9Cr-1W2Mn</td>
<td>12Cr-1W6Mn</td>
<td>neutrons (FPI/MAFA)</td>
<td>NR</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT-9</td>
<td>neutrons (EBR II)</td>
<td>2.4 x 10⁻⁷</td>
<td>13</td>
<td>410 - 465</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-P, S, C</td>
<td>neutrons (LAMPF A-6)</td>
<td>NR</td>
<td>0.005</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JFMS</td>
<td>Fe-10Cr</td>
<td>1.125 MeV e⁺</td>
<td>4.8 x 10⁻⁴</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Fe-10Cr-1Ni</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-10Cr-5Ni</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIN 1.4914</td>
<td>6.3 MeV H⁺</td>
<td>NR</td>
<td>0.06,0.64</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12G05N05Mn + P, Si, Mo, V</td>
<td>1 MeV e⁻</td>
<td>2.7 x 10⁻³</td>
<td>10</td>
<td>350 - 600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NR = not reported ↑ = solute enriched ↓ = solute depleted
Mahon [174] also observed nickel enrichment, which was enhanced by the presence of silicon. Muroga et al [172] found there to be a dependence on sink type: nickel was enriched at interstitially biased sinks and depleted at neutral sinks.

Manganese was variously reported to be enriched or depleted. In a binary alloy Takahashi et al [160] found manganese depletion; in a series of ternary iron-chromium-manganese alloys [163] they detected enrichment of manganese. Kimura et al [169] and Jung and Klein [173] observed its enrichment in 12%Cr steels. Clausing et al [170], Muroga et al [172], Brimhall et al [166-168] and Mahon [174] reported no manganese segregation effects.

Silicon was found either not to segregate, Brimhall et al [166-168], or otherwise always to be enriched: Kimura et al [169], Clausing et al [170], Muroga et al [172], Jung and Klein [173] and Mahon [174].

Phosphorus was also always found to be enriched at sinks when segregation occurred, although Ohnuki et al [162] and Brimhall et al [168] found the segregation to disappear at high doses owing to surface effects. It should perhaps be pointed out that in the commercial steels investigated, where phosphorus is an unwanted impurity, its concentration is so low that depletion would not be detectable, even if it did occur.

Mahon [174] found vanadium to be depleted at grain boundaries under ion irradiation, but enriched under electron irradiation. Takahashi et al [165] also reported vanadium enrichment at dislocation loops following electron irradiation.

Molybdenum depletion at voids was detected by Takeyama et al [164] and at grain boundaries by Mahon [174]. No effect was reported in the commercial grade 12%Cr steels.

2.5 Experimental methods

A brief discussion will be made of the experimental methods used to generate and determine radiation-induced segregation in the previously reported studies.

2.5.1 Irradiation

2.5.1.1 Electron irradiation

Electron irradiation is the most easily performed. Thin foils are prepared in the usual way and bombarded with electrons, typically of 1 MeV energy. Very high damage rates are
possible - of the order of $10^{-3}$ dpa/s. Electron irradiation does not impart great energy to the PKA and so there are almost no displacement cascades. As such, electron irradiation is a very efficient means of generating freely migrating defects. As a consequence of the damage rate being orders of magnitude greater than for neutron irradiation, there is an associated shift in the temperature at which peak radiation effects occur. Therefore, studies performed at a particular temperature using electron irradiation would correspond to a lower temperature for neutron irradiations.

Since the irradiation is performed using thin foil specimens, surface effects are important when using electron irradiation for the generation of radiation induced segregation. The surfaces act as perfect sinks for point defects and the foil thickness will, in general, be less than the distance between sinks of interest. Point defect fluxes to the surfaces will be introduced and thus interfere with the segregation process of interest. Any radiation-induced segregation to sinks such as grain boundaries will be masked by surface segregation. A further disadvantage of HVEM electron irradiation is the nature of the electron beam itself. It is not of uniform intensity, instead being approximately Gaussian, or bell shaped, in profile. Consequently a non-uniform generation of point defects results, and hence point defect fluxes are set up even in the absence of sinks. This non-uniform irradiation thus superimposes its own radial solute redistribution on any effects at sinks, as discussed and modelled by Lam et al [140-142].

### 2.5.1.2 Ion irradiation

Ion irradiation is also an accelerated form of simulation for radiation damage studies. Typical dose rates are $10^{-4}$ dpa/s, giving a factor of $10^2$ to $10^4$ increase over the rate of damage in nuclear reactor cores. There is also a temperature shift for ion irradiation studies to scale to neutron irradiation. Heavy ion irradiation damage is concentrated principally in a very narrow volume close to the the target's surface. The damage varies axially with depth during heavy ion irradiation and the surface also acts as a sink. This may be advantageous if surface segregation studies are to be performed by AES - but the sputtering away of the surface layers during irradiation can simultaneously remove any segregant, as discussed in the previous section. If surface effects are not to be examined, the surface layer is usually removed and specimens back-thinned to produce foils for subsequent EDX analysis. Samples are non-active after heavy ion irradiation, which greatly facilitates specimen preparation and handling.

The technique simulates the total damage a material may accrue under neutron irradiation, including displacement cascades, but does not simulate long term thermal exposure as in-reactor. The technique also subtly alters the generated point defect population by
effectively injecting an extra interstitial atom for each implanted ion, regardless of any other point defects it creates in so doing. This effect is relatively greater for lower energy light ion irradiation, since the displacement cascades, and hence number of defects created per ion, are smaller. Mazey has recently reviewed the use of ion-beam irradiation simulation techniques [176].

2.5.1.3 Neutron irradiation

The determination of radiation-induced segregation from neutron irradiated material obviously has advantages. The damage is not simulated since the material is in an as-service condition, and thus no temperature correlation effects are necessary. Neutron irradiation produces almost uniform damage so that bulk specimens may be irradiated then fractured and analysed by AES if desired. However, damage rates are very low; a year spent in the core of a fast breeder reactor will typically generate a total damage of about 30 dpa at a rate of $10^{-6}$ dpa/s. Thus very long exposure times are necessary to produce highly dosed specimens which is expensive. Handling and specimen preparation is then problematical, as will be evident later, since transmutation events make most steels highly active (dependent upon composition).

2.5.2 Analysis techniques

The two general techniques used for the analysis of radiation-induced segregation in ferritic steels reported above are the surface analysis technique of Auger electron spectroscopy (AES) and STEM-based energy dispersive X-ray analysis (EDX). The relative merits and deficiencies of these methods will be discussed briefly below; the more particular technique of EDX by use of a field emission gun scanning transmission electron microscope (FEGSTEM) will be discussed in more detail in Section 3.6.1.

2.5.2.1 Auger electron spectroscopy

The mean free path, and hence escape depth, of Auger electrons is typically less than 1 nm. Consequently the generation and detection of Auger electrons is a very surface specific analysis technique. If ion-beam milling is combined with the spectroscopy of Auger electrons, surface layers can be sequentially analysed chemically and removed to construct compositional depth profiles. Radiation-induced segregation to grain boundaries may be analysed by AES if the boundaries can be exposed as a free surface. This may be done by cryogenically fracturing embrittled ferritic materials in situ. The technique possesses excellent depth resolution, but does have a number of disadvantages for examining radiation-induced segregation.
The volume of material required for fracture and subsequent analysis by this technique rather necessitates neutron irradiated, instead of electron or ion irradiated, material. This is not inherently a disadvantage, since it is neutron irradiated material that is of ultimate interest. However the associated activity of neutron irradiated bulk specimens makes handling difficult. Moreover, since the depth profiling technique is essentially destructive, possibly unacceptable contamination of the equipment may result. This aside, the major disadvantages lie with the exposing and analysis of the boundaries themselves. Intergranular fracture, particularly of austenitic stainless steel, is not always achievable; even if it is, the exposed boundaries are chosen by the fracture process, not the investigator. Also, by its very nature, the technique examines compositional depth profiles of only one side of a boundary. The second side will be contained in the other fracture piece and will be extremely difficult, if not impossible, to match. Furthermore, the relatively poor lateral resolution (tens of nanometers) and imaging of the technique means that small boundary precipitates may be included within the analysed volume, making interpretation difficult.

2.5.2.2 Energy dispersive X-ray analysis by STEM

The geometry of analysis by STEM-based EDX is quite different to that by AES. Instead of boundaries being normal to the beam, as in AES, they are oriented parallel to the beam. Spatial compositional profiles are generated by suitably positioning the incident electron beam to varying distances from the boundary plane and collecting the resultant X-ray spectra. Clearly, the meaningful spatial resolution of the technique is determined by the volume of electron excited material. This in turn, for a specific material, is dependent upon both the incident electron probe diameter and the degree of high angle elastic scattering of the beam through the foil thickness. For an infinitely thin foil the incident probe diameter places the lower limit on the attainable spatial resolution, which is progressively increased by the beam broadening effect with increasing foil thickness.

All the cited studies of radiation-induced segregation in ferritic materials have used microscopes with conventional illumination, that is tungsten hairpin or LaB₆ filaments. The practical minimum probe size in these instruments is constrained by the statistical and drift requirements to generate sufficient X-ray counts in reasonable times. The minimum usable probe sizes are usually 10 to 20 nm in diameter as seen from the values quoted in Table 4. Low temperature radiation-induced segregation is often on a scale less than this. For instance, results from an austenitic stainless steel neutron irradiated at 354°C, Norris et al [177], show the full width half maximum values of compositional profiles to be 3.5 to 6.5 nm. Clearly for probe diameters greater than the width of the segregated layer, any concentration profile determined is as much a measure of spatial probe current
distribution as of spatial compositional variation. Relatively coarse probes may detect segregation to interfaces, but the fraction any segregated layer contributes to the X-ray signal diminishes approximately as the square of the probe size. The sensitivity of the technique is therefore reduced for increasing probe diameters and the spatial resolution of raw data production is clearly inferior to the depth resolution of AES.

The advantages of STEM-based EDX analysis of radiation-induced segregation in irradiated material are several. The technique is applicable to analysis of material irradiated by electrons, ions or neutrons. The small volume of material required is advantageous for highly active neutron irradiated specimens although, as we shall see, the technique is not devoid of problems in this respect. Furthermore, analysis of the specimen is non-destructive and, with suitable precautions, may take place in microscopes not specifically reserved for active use. The most fundamental advantage of the technique, however, is the ability to unambiguously select any desired sink type for analysis, including precipitate-free segments of grain boundaries.

2.6 Precipitation evolution under irradiation

Whilst this thesis is not principally concerned with the characterization of precipitate evolution during irradiation, the chemical composition of any radiation-induced precipitation can offer indirect evidence of radiation-induced segregation. Any segregation to sinks causes 'microalloy' regions of different composition to the matrix. Precipitate formation in such regions may be of significantly different composition, or even of phases not observed during thermal ageing of the bulk composition. Williams and Titchmarsh [178] have demonstrated this behaviour by thermally ageing Type 316 steel compositionally modified to mimic the effects of radiation-induced segregation at sinks. Instead of the usual $M_{23}C_6$ or $M_6C$ formation, G phase was found during ageing - as observed during irradiation of Type 316 steel.

Several workers [60,61,179-187] have investigated precipitate development in 12%Cr steels during irradiation and their results on the formation and stability of radiation-induced phases have recently been reviewed by Maziasz [188]. A number of radiation-induced phases have been observed to form, falling into one of two categories according to their manifestation. Most 12%Cr alloys develop a very fine (2-20 nm) intragranular precipitate during neutron irradiation at between 400 and 500°C: phases thus observed constitute the first category. The second category consists of phases found only occasionally in some 12%Cr steels, or present only in trace quantities. Radiation-induced precipitate phases belonging to both categories and their approximate compositions are shown in Table 5.
## Table 5

Typical compositions of precipitate phases observed in irradiated 12%Cr steels

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition (at.%)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>P</td>
</tr>
<tr>
<td>M₆C</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td>G</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>16</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>M₂(X)</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>M₃P</td>
<td>-</td>
<td>bal.</td>
</tr>
<tr>
<td>MP</td>
<td>-</td>
<td>bal.</td>
</tr>
<tr>
<td>M₂₃C₆*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Laves*</td>
<td>10</td>
<td>4</td>
</tr>
</tbody>
</table>

* Phases present in unirradiated material.
The actual precipitate phase evolution during neutron irradiation is very sensitive to alloy composition and even to tempering conditions \[61\]. Binary iron-chromium alloys tend to form \(\alpha'\), whereas steels containing vanadium, niobium or tungsten usually exhibit \(M_6C(\eta), \chi\) or \(G\) phase formation. The phases from the first category are generally mutually exclusive in that the fine intragranular precipitate is not usually a mixture of phases. The radiation-induced phases fitting into the second category in the 12\%Cr steels are the needle-like \(M_2X\), the globular or sheet-like \(\sigma\), needle-like \(M_3P\) and the globular MP.

It can be seen from Table 5 that, compared with the matrix composition, phases from the first category commonly observed in 12\%Cr steels (\(M_6C, \chi\) and \(G\) phases) are all particularly enriched in nickel and silicon. Moreover, Laves phase formation (the usual phase observed after thermal ageing of 12\%Cr steel) is found to be suppressed by irradiation \[61.181\]. If the typical composition of Laves phase is also compared with that of \(M_6C, \chi\) and \(G\) phase it is apparent that the radiation-induced phases are consistently richer in nickel and silicon and leaner in molybdenum. Maziasz \[188\] draws attention to the fact that all the radiation-induced phases are chromium-rich with respect to the matrix (and, incidentally, to Laves phase), the singular exception being \(G\) phase. He suggests that either chromium supersaturation or segregation, or both, are responsible. Thermal ageing studies of 9Cr1MoVNb steel in comparison with irradiated material provide further evidence of chromium enrichment \[61\]. The MC precipitates, which are vanadium-rich after tempering and thermal ageing, become very rich in chromium at the expense of vanadium during irradiation. The appearance of chromium-rich precipitates during irradiation, at odds with most reports of the direction of chromium segregation during irradiation, may be explained by chromium supersaturation. Dissolution of existing \(M_{23}C_6\) and \(M_2X\) (containing 70-75\%Cr and 80-90\%Cr respectively) has been observed during irradiation of a plain 12\%Cr steel \[60\]. The radiation-induced phase \(M_6C\), although richer in chromium than the matrix, actually contains less chromium than the phases it replaces.
3.1 Material

The base material used for this work was FV448, a commercial grade 12%CrMoVNb steel of actual composition as given in Table 6. The stock material was in the form of 2.5 mm thick coupons, originating as offcuts from quarter thickness Charpy specimens. The coupons were encapsulated in silica vials filled with low pressure argon to prevent oxidation during the heat treatment schedule. The manufacturer's recommended heat treatment schedule for this material has been modified to optimize the microstructure for fast reactor wrapper applications [9], where formability is a key requirement and maximum high temperature strength less so. Solution treatment at 1100°C for 1 hour was followed by an air cool to produce a fully martensitic structure. This was subsequently tempered for 6 hours at 750°C and air cooled. This was the starting condition of all the parent plate material.

Modified weld metal specimens were produced from plates of FV448 in the half tempered condition (1 hour at 1100°C, AC + 3 hours at 750°C, AC). These plates were butted together and MIG welded. The fusion zone was made off-normal in composition by the addition of small quantities of the nickel-rich alloy PE16 (Table 7) as filler material during welding. Specimens incorporating the fusion zone were machined transversely from the welded plate, encapsulated and post-weld heat treated for 6 hours at 750°C.

3.2 Irradiation

Neutron irradiations were performed in the core of the Prototype Fast Reactor (PFR) at Dounreay. Two sets of both parent plate and weld zone material specimens were placed in sodium filled capsules in experimental tube sites in the reactor core. The target irradiation temperatures for the two sets were 420 and 500°C respectively. However, the effects of the cyclic nature of the operation of PFR and the temperature gradients within the reactor core impose temperature fluctuations on the specimens during their irradiation. The actual details of the irradiation history of the two experimental sites are given in Table 8. The actual dose weighted average temperatures achieved were approximately 400 and 465°C respectively. The total neutron fluence the parent plate material was exposed to corresponded to total damage levels of 33 dpa (NRT) at 400°C and 50 dpa (NRT) at 465°C. From Table 8 this corresponds to dose rates of $1.1 \times 10^{-6}$ dpa/s and $1.7 \times 10^{-6}$ dpa/s respectively. The total times at temperature in the reactor were 12000 hours at an average of 386°C and 16944 hours at 444°C respectively. For the weld metal material,
### Table 6
Chemical compositions of FV448 parent plate and off-normal weld metal (wt.%).

<table>
<thead>
<tr>
<th>FV448</th>
<th>Fe</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate</td>
<td>bal.</td>
<td>0.10</td>
<td>10.65</td>
<td>0.64</td>
<td>0.38</td>
<td>1.01</td>
<td>0.64</td>
<td>0.16</td>
<td>0.3</td>
<td>0.016</td>
<td>0.006</td>
</tr>
<tr>
<td>Weld*</td>
<td>bal.</td>
<td>NA</td>
<td>13.3</td>
<td>4.7</td>
<td>0.5</td>
<td>0.8</td>
<td>0.8</td>
<td>0.1</td>
<td>0.3</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

* based on EDX measurements

NA = Not analysed

### Table 7
Nominal chemical composition of PE16 (wt.%).

<table>
<thead>
<tr>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>43.5</td>
<td>34</td>
<td>16.5</td>
<td>3.3</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>
### Table 8

Irradiation history of FV448 parent plate material.

(i) Target irradiation temperature : 420°C
Time-weighted average temperature : 386°C
Dose-weighted average temperature : 399°C
Temperature range : 309 to 425°C
Total time in reactor : 12000 hrs
Total effective full power time : 8424 hrs
Total displacement damage level : 33 dpa (NRT)
Effective displacement damage rate : $1.1 \times 10^{-6}$ dpa/s

(ii) Target irradiation temperature : 500°C
Time-weighted average temperature : 444°C
Dose-weighted average temperature : 463°C
Temperature range : 319 to 483°C
Total time in reactor : 16944 hrs
Total effective full power time : 8256 hrs
Total displacement damage level : 50 dpa (NRT)
Effective displacement damage rate : $1.7 \times 10^{-6}$ dpa/s
3.3 Thermal treatments

3.3.1 Long term ageing

To enable radiation effects to be distinguished from any purely thermal effects resulting from time spent at elevated temperature during irradiation, thermal control specimens were produced. Encapsulated as-tempered parent plate material was aged at 400°C for 6840 hours and at 465°C for 6336 hours. Similarly, as-tempered weld zone material was aged at 400 and 465°C for 4656 hours to simulate the effects of prolonged elevated temperature service.

3.3.2 Post-irradiation annealing

Subsequent to their irradiation, specimens of the parent plate material were annealed at the relevant irradiation temperature for 1000 hours. This post-irradiation annealing treatment was also designed to distinguish any radiation-induced effects from thermal ones. However, the continued presence of any effects thought to be induced by irradiation following this treatment does not automatically preclude them from being products of the irradiation, since thermal diffusion at these relatively low temperatures is sluggish.

3.4 Thin foil preparation

Thin foil specimen preparation for electron microscope examination is usually a fairly routine technique. However, the specimens became extremely radioactive themselves owing to transmutation events during high dose neutron irradiation, in contrast to ion and electron irradiation simulations. Not only does this make handling and preparation by the conventional method much more difficult, but because the specimen activities were so high, the conventional technique proved unsuitable for the preparation of foils for EDX analysis, and had to be modified as detailed below.

3.4.1 Inactive material

Because of the problems associated with active material handling, some time was spent developing a consistent thin foil preparation technique with inactive material. The procedure followed was to cut from the 2.5 mm thick material 5 slices approximately 0.5 mm thick, using a low speed diamond saw. From these slices, 3 mm discs were trepanned by a spark erosion machine equipped with a tubular electrode. These discs were wet ground on successively finer grade silicon carbide paper to a thickness of about 150 μm. Final thinning and perforation was performed using a Struers Tenupol twin jet electropolishing machine. Good thin foils were found to be consistently produced by using an electrolyte of 10% perchloric acid, 70% absolute ethanol and 20% glycerol, cooled by liquid nitrogen to -10°C. The operating voltage used was 20 V, resulting in a
current of 30 to 40 mA. The electrolyte flow was set to maximum for the first minute of electropolishing to dimple the disc, then reduced to a lower rate until perforation occurred. The thin foils were then cleaned in acetone and stored under absolute alcohol.

3.4.2. Active material

The activity of the material after irradiation in PFR was such that the initial cutting operation to produce a volume of material approximately 10 x 5 x 2.5 mm had to be done remotely in-cell. The activity of even this volume of material was sufficient to give a radiation exposure of 3 mSv hr\(^{-1}\) at 30 cm; this compares with a statutory annual limit for non-classified radiation workers of just 5 mSv. Therefore the material must be kept as far away as possible during handling, using as long a pair of tongs or tweezers as practicably possible. The time spent in the vicinity of the active material was reduced to the minimum necessary to set up the slicing, grinding or polishing operation.

Since the production of thin foil specimens is essentially one of material removal, all the processes were performed in sealed glove boxes to contain the spread of contamination. The glove boxes were shielded with lead to a thickness of 5 or 10 cm in order to reduce the radiation reaching the torso when working at the box-face. Hands and arms are inserted into the glove box interiors unshielded and hence thermo-luminescent finger monitors were used to check exposure. Moreover, a whole body dose limit was set such that once it had been reached no further work with active material was allowed that day. Fortunately, with care, most operations could be completed within the dose limit. Although the material was successively reduced in volume when producing a thin foil, and thus its activity lowered, the necessary manoueveres became more intricate, involving closer and longer handling of the material.

A low speed diamond saw was used to produce slices of material approximately 0.5 mm thick in a first glove box. Once set up this could be left to operate remotely. Each slice had an activity of about 400 \(\mu\)Sv hr\(^{-1}\) at 30 cm. Again, spark erosion machining was used to trepan 3 mm diameter discs from the sliced material. After each disc was cut it was removed from the second glove box to reduce the total activity within the box for successive trepanning operations. Each of these 3 mm discs was then wet ground from roughly 500 to 150 \(\mu\)m thickness in a third glove box by the use of progressively finer grade silicon carbide papers. This operation had the greatest potential for contamination since the volume of material is reduced by two thirds in the form of grindings. After just two specimens have been ground in this way, the contribution of the grindings to the background activity is greater than the activity of each specimen being ground. Frequent decontamination of the box is therefore necessary to prevent undue radiation exposure.
Final thinning and perforation to produce thin foils was initially carried out on these 3 mm discs using similar electropolishing equipment and the same conditions as for inactive thin foil preparation described above. The method was successful in producing thin foils suitable for TEM examination, but which were found to be unsuitable for quantitative EDX analysis. The high residual activity of the thin foils, about 150 \( \mu \text{Sv hr}^{-1} \) at 10 cm, resulted in complete saturation of the X-ray detector. Thus chemical analysis of these active conventional 3 mm thin foils by EDX proved impossible.

### 3.4.3 Reduced activity thin foil preparation

Most of the volume of a conventional 3 mm thin foil specimen is concentrated at its periphery. This outer rim is important only in conferring mechanical stability to the foil, and yet with active material it contributes the bulk of the specimen's radioactivity. Rose and Rowe [189] at the Berkeley Nuclear Laboratories have developed a technique whereby a 1 mm disc of active material is placed within an annulus of unirradiated material. This composite disc is then thinned in the usual manner. However, preferential dissolution of the interface often takes place such that specimen perforation does not always occur in the body of the active material. Furthermore, the joint coupling the active and inactive material is not mechanically sound. This is a potential problem for ferromagnetic materials, of interest here, since the intense magnetic fields generated by electron microscope objective lenses could rip the central portion of active material from its surrounding annulus. Dumbill and Fuller [190] of Harwell Laboratory have outlined an electroplating technique which they used to overcome these problems. This is the basis for the technique developed in this work.

The initial preparation is the same as for conventional 3 mm discs. From a 3 mm diameter disc of active material ground to about 150 \( \mu \text{m} \) are punched three 1 mm diameter discs using a specially manufactured jig. These active 1 mm diameter discs formed the central portions of the composite discs, which were built up by electroplating nickel around them. The electroplating procedure was as follows.

An aluminium backing plate, about 20 x 25 mm, was held between the points of a pair of tweezers which were then taped shut to clamp the plate. A thin, even layer of silver DAG paint, greatly diluted by amyl acetate, was applied to one side of the aluminium plate. Lacomit solution was then painted over the reverse side of the plate, the prong of the tweezers and the edges of the DAG covered side of the plate to leave a region roughly 15 x 20 mm uncovered. The 1 mm diameter discs were first cleaned ultrasonically in acetone to ensure a clean interface for the nickel to key on to. They were then dipped into the solvent amyl acetate and placed individually onto the DAG covered backing plate,
Table 9
Compositions of electroplating solutions.

<table>
<thead>
<tr>
<th>Compositions of Electroplating Solutions</th>
</tr>
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<tbody>
<tr>
<td><strong>Striking solution:</strong></td>
</tr>
<tr>
<td>NiCl₂</td>
</tr>
<tr>
<td>HCl</td>
</tr>
<tr>
<td>make up to 1 litre with distilled water</td>
</tr>
<tr>
<td><strong>Watts bath:</strong></td>
</tr>
<tr>
<td>NiSO₄</td>
</tr>
<tr>
<td>NiCl₂</td>
</tr>
<tr>
<td>H₃BO₃</td>
</tr>
<tr>
<td>CH₃(CH₂)₁₁OSO₃Na</td>
</tr>
<tr>
<td>H₂O₂</td>
</tr>
<tr>
<td>make up to 1 litre with distilled water</td>
</tr>
</tbody>
</table>
Figure 3.1: Electroplated nickel layers embedding 1mm discs, showing an early heavily pitted example (left) and a sound layer produced by the modified electroplating process (right).

Figure 3.2: Die-stamped 3mm disc from which three 1mm discs have been obtained (left), and a composite 3mm disc with a 1mm disc of the material of interest forming its central portion (right).
well spaced out from each other, so that in total five or six discs were stuck onto the backing plate. This assembly formed the cathode, whilst a pure nickel bar was used as the anode.

Two stages of electroplating were used. The first stage was to deposit a thin 'strike' layer of nickel onto the cathode assembly using a striking solution of composition given in Table 9. A current of 290 mA was passed through the electrolyte at room temperature for one minute. The second electroplating stage laid down the thick layer of nickel, embedding the 1 mm diameter discs within it. A modified Watts bath of composition given in Table 9 was used. Initially hydrogen evolution at the cathode was a severe problem, causing a porous and pitted deposit. Commercial nickel electroplating operations rely primarily upon agitation to remove adhering bubbles by either vigorously bubbling air through the electrolyte or shaking the articles being electroplated. A small quantity of hydrogen peroxide and a wetting agent are often also added. In this case a magnetic stirrer was used to agitate the electrolyte, with a few drops of hydrogen peroxide added to the plating bath just before the commencement of plating. A wetting agent, in the form of sodium lauryl sulphate, was also found to be beneficial for the efficient removal of hydrogen bubbles. The electrolyte was heated to 50°C and the plating carried out overnight with a current of 400 mA to form a plated layer about 300 - 500 µm thick incorporating the 1 mm diameter discs.

The electroplated layer was then prised off the backing plate with the active discs embedded. Figure 3.1 shows an example of an early, pitted electroplated layer and a later example of a sound, unpitted layer. From such an electroplated layer 3 mm diameter discs were trepanned, centred over the 1 mm diameter active disc. The nickel protrusion was ground back to just reveal the central 1 mm diameter disc and this composite 3 mm diameter disc then ground back from the underside to a thickness of 150 µm. An example of such a composite disc, together with the original 3 mm disc from which the 1 mm discs were punched is shown in Figure 3.2.

This composite disc could then be electropolished in the standard way, as above, to produce a thin foil specimen in which the volume of active material is reduced greatly compared with a conventional thin foil, thus allowing EDX analysis to be performed. An additional benefit of this technique is the concomitant reduction in ferromagnetic mass from the thin foil, allowing full correction of objective astigmatism and easier tilting. For this reason, thin foils of inactive material were also made from composite discs.
3.5 Transmission electron microscopy

The thin foils were examined in a Philips EM430 TEM equipped with a LaB$_6$ source operating at 300 kV. Five foils prepared for each material condition were initially assessed according to their suitability for subsequent segregation analysis with regard to the presence of the desired sink types within the thin area and its extent. The two best foils for each material condition were selected for further analysis using the FEGSTEM. The microstructures were characterized in general with regard to radiation-induced modification. A detailed analysis of dislocation structure evolution and precipitate development was not performed since this has been done for this material under similar irradiation conditions [60,191].

The irradiated weld metal specimens exhibited a gross non-equilibrium phase transformation product. This was characterized extensively, with the orientation relationships between it and the matrix determined in detail. The ferromagnetic nature of the specimens did not ease this task; moreover, problems were experienced with the goniometer tilt being effectively restricted to just 30° because fouling of the specimen by the objective aperture occurred at greater tilts. Moving the specimen from the eucentric height did little to alleviate this.

3.6 Microchemical analysis

The instrument used to measure spatial chemical composition was the Vacuum Generators HB501 field emission gun scanning transmission electron microscope (FEGSTEM). There are very few of these machines in use worldwide, but it offers advantages over conventionally illuminated STEM's for high resolution chemical analysis. As such it warrants a brief description; for a more detailed description see references [192,193].

3.6.1 VG HB501 FEGSTEM

The main external features of the microscope are shown in Figure 3.3 with the electron optical column, the main control panel and the interfaced Link Analytical microanalyser in view. Hidden from view is the retractable X-ray detector assembly and the vacuum control unit. A schematic cross-section of the electron optical column is shown in Figure 3.4.

In contrast to a conventional TEM/STEM configuration, the electron source is situated below the specimen with the electrons travelling up the column to the specimen and array of detectors. The source itself is a cold field emission gun, consisting of an oriented
Figure 3.3: View of the external features of the VG HB501 FEGSTEM, showing the electron optical column, main control panel and Link Analytical microanalysis unit.
Figure 3.4: Schematic cross section of the electron optical column of the VG HB501 FEGSTEM.
tungsten single crystal having a (310) zone axis parallel to the optical axis. A first anode held at 3-4 kV positioned close to the tip extracts electrons by tunnelling through the crystal surface potential barrier. The second anode accelerates the electrons to 100 kV. For stable electron emission a gun chamber vacuum of better than $10^{-10}$ torr is required; the HB501 has a guaranteed gun chamber pressure of better than $5 \times 10^{-11}$ torr. Even so, focussing of contaminant gas ions can cause tip instabilities. To overcome this, the tip extraction voltage is periodically switched off and a heating current passed to drive off adsorbed gas atoms.

Working up the optical column, the gun lens initially focusses the beam producing a crossover near the plane of the differential pumping aperture. The gun lens is not beneficial for the finest probes, since its function is to increase beam current in probe sizes greater than 3 nm diameter. The differential pumping aperture can maintain a pressure difference of $10^3$ between the gun chamber and the rest of the microscope, which typically has a vacuum of $10^{-9}$ to $10^{-8}$ torr.

A double condenser lens system is used to transfer the image of the source to the plane of the selected area diffraction aperture (SADA). The double condenser allows in principle the variation of any two of the three parameters of beam current, probe size and convergence angle, whilst keeping the third constant. In practice the fixed parameter is governed by the field limiting aperture. If the objective aperture (OA) is chosen then the convergence angle is fixed, whereas the beam current is constant if the virtual objective aperture (VOA) is limiting. Use of the OA results in a spurious X-ray signal, hence for EDX work a VOA and a small SADA are used.

For aberration-free imaging of the electron source, the probe current is given by [194]:

$$i = \pi^2 \alpha^2 d^2 B / 4$$

where $\alpha$ is the convergence angle, $d$ is the probe diameter and $B$ is the source brightness. Hence under conditions for EDX work, where a VOA is employed thus fixing the beam current, the probe diameter is inversely proportional to the convergence angle:

$$d = \frac{2}{\pi \alpha} \sqrt{\frac{i}{B}}$$

Spherical aberration limits the minimum attainable beam diameter at high convergence angles, obeying the following relationship:

$$d_r = \frac{1}{2} C_4 \alpha^3$$
Figure 3.5: Theoretical variation in electron probe diameter, $d$, with convergence angle, $\alpha$, for a variety of first condenser settings ($C_1$) on the VG HB501 FEGSTEM at 100 kV and a beam current of 0.85 nA, estimated by adding in quadrature the contributions from diffraction, spherical aberration and Gaussian demagnification [192].
where $C_s$ is the coefficient of spherical aberration. Diffraction effects also limit the minimum beam diameter according to the following relationship:

$$d = 1.22\frac{\lambda}{\alpha}$$

where $\lambda$ is the wavelength of the electron beam. These three criteria can be added in quadrature to provide a theoretical variation of probe size with convergence angle. This theoretical variation is shown in Figure 3.5 for the electron optical conditions of the HB501 [193]. Under conditions typical for EDX work, the minimum attainable probe diameter is 2.3 nm for a current of 1 nA. For the same convergence angle and beam current, the aberration-free Gaussian probe diameter will be greater by a factor of 14 for a LaB$_6$ source and by a factor of 45 for a thermionic tungsten filament (assuming brightnesses of $10^7$, $5 \times 10^4$ and $5 \times 10^3$ A/mm$^2$/sr for cold field emission, LaB$_6$ and tungsten sources [194] respectively). This orders of magnitude increase in brightness is the key to the FEGSTEM's ability to produce extremely fine probe sizes, yet which contain sufficient current for statistically significant X-ray generation in reasonable collection times.

The specimen holder fits into a top entry stage, immersing the foil in the high excitation objective lens field. A special single tilt holder is necessary for the examination of ferritic foils, since the very strong interaction between the objective lens field and ferromagnetic specimens has been found to damage the gimbal mechanism in a conventional double tilt holder. The specimen holder gimbal assemblage is of beryllium construction to minimize background X-ray generation.

The absence of post-specimen lenses results in space for a variety of detectors. The first of these is a retractable fluorescent screen angled at 45°, used to view the diffraction pattern. The annular dark field detector is linked to a photomultiplier and the visual display units of the microscope. This collects electrons scattered from the incident electron beam to quite high angles and is useful for imaging precipitates. The bright field detector and the electron spectrometer collect electrons close to the optic axis for bright field imaging and electron energy loss spectroscopy. The original electron energy loss spectrometer was a serial device and is currently being replaced by a parallel collection device which offers significant benefits for high resolution microanalysis.

In this work, the energy dispersive X-ray microanalysis system was used. The X-ray detector is a Link Systems LZ-5 retractable windowless Si(Li) crystal subtending the high solid collection angle of 0.181 sr. The absence of a beryllium window allows detection of all elements in the periodic table down to boron (atomic no.5). It is the very low column pressure in the HB501 that allows the use of a windowless detector without
condensation and contamination of the crystal rapidly deteriorating performance. Typically the detector may be used for about twelve months between decontaminating by a crystal warm-up procedure. The detector has good resolution for an energy dispersive system, of approximately 90 eV full width half maximum (FWHM) of the strobbed zero energy peak.

The data analysing system is the Link Systems AN10000 X-ray microanalysis system. In addition to straightforward collection, manipulation and quantification of X-ray spectra, the system may be used to drive the electron probe to generate linescans or acquire elemental X-ray maps and digital electron images. These can subsequently be manipulated by a digital image processing and display package which allows image analysis to generate, for example, histograms and line profiles, and image processing which may be used to enhance the raw image.

3.6.2 Procedure

The specimen under examination was, whenever possible, taken from storage under absolute ethanol, mounted in the holder and inserted into the specimen stage of the microscope the night before intended analysis. This allowed the specimen to settle and minimized drift at the start of analysis the following day. For analysis a suitable interface of the desired type was selected and oriented so that its plane was parallel to that of the incident electron beam. This often took some time, since a precipitate-free section of boundary already nearly aligned to the electron beam and favourably oriented about the tilt axis in a thin section of the foil was required. A precipitate-free section of boundary is necessary to avoid precipitation effects and limit the mechanism of solute redistribution to that of segregation. The boundary section must be nearly aligned to the beam prior to tilting it exactly parallel, since there is only a limited angle of tilt available to work with for EDX analysis, defined by line-of-sight between the analysis point and detector. For ferritic foils, tilting range is also constrained by the range over which objective astigmatism can fully be corrected. The use of the single tilt holder also requires the boundary section to be roughly parallel - or at least not perpendicular - to the tilt axis so that the boundary may be tilted successfully into the plane of the electron beam. The boundary section should also ideally lie in a thin portion of the foil to minimize beam broadening effects which degrade the spatial resolution of the analysis. A typical boundary section used for analysis is illustrated in Figure 3.6, showing the projected width of the boundary plane to be less than 2 nm in the bright field image.

Spatial compositional data across various interfaces were obtained by placing the stationary electron probe at the required analysis point and collecting an EDX spectrum
Figure 3.6: (a) FEGSTEM image of a typical boundary analysed, (b) oriented parallel to the incident electron probe and precipitate-free at the point of analysis.
for 100 seconds live time. Count rates of 1400 cps for active foils and 1000 cps for inactive foils were typical, with respective dead times of 40 and 30%. Spectra were obtained for points on the boundary plane and at distances of 2.5, 5, 10, 50 and 100 nm either side.

3.6.3 Specimen analysis considerations

3.6.3.1 Drift

Working at very high magnification (2,000,000 x) with a very fine probe (~3-4 nm) places a severe constraint on the specimen stability if drift is not to be the factor limiting the attainable resolution. Drift can arise from fluctuations in cooling water temperature, specimen holder instability, beam heating, room vibrations and stray electromagnetic fields. Specimen drift was corrected by periodically halting data acquisition to examine the beam position relative to a reference point and repositioning if necessary. Drift was kept to within about 0.5 nm when analysing compositions between 5 nm either side of the interface. If the specimen was found to have drifted by more than this between successive checks, the spectrum was discarded and started afresh.

3.6.3.2 Contamination

Contamination is a further barrier to good microanalysis. Radiation damage of adsorbed hydrocarbon molecules on the specimen surface results in a carbon-rich cross-linked structure under the electron beam.

This contaminant becomes particularly evident if using very fine probes, when a contamination needle is produced. Surface diffusion of hydrocarbons allows the needle to continue to grow under the electron probe. The effect can be deliberately used to advantage in foil thickness measurements. However, for microanalysis the presence of such contamination needles is deleterious. The contamination needle can easily more than double the effective specimen thickness under the electron probe. Elastic scattering can therefore broaden the beam before it even reaches the specimen surface and its exit diameter will be further increased, resulting in a loss of spatial resolution. Beam broadening is not simply a linear function of specimen thickness; single scattering approximations predict a dependence on thickness to the power 3/2 [195]. Additionally, the growth of contamination peaks eventually obscures image detail, which can be a particular problem when analysing the composition at closely spaced points near to the interface.
Fortunately, the windowless X-ray detector is capable of measuring carbon K-line X-rays and the height of this peak allows the extent of carbon build up to be monitored before it actually becomes visible in the image. To minimize contamination the specimen is 'flooded' with electrons before analysis of an interface begins and also once the carbon K\_\alpha peak is observed to be increasing significantly. The apertures are removed and the magnification reduced so that an intense beam of electrons sweeps across a large portion of the foil. Any adsorbed hydrocarbons under the beam are cross-linked and thus fixed in the scanned area. For any contamination spike to grow, surface diffusion across the foil from outside the scanned area or further adsorption must occur.

3.6.3.3 Specimen thickness

The specimen thickness at the point of analysis is primarily determined by the location of a suitable boundary section, rather than by the operator. However, some consideration must be given to the local specimen thickness. Thick areas lead to considerable broadening of the incident electron beam as it travels through the foil. Consequently there is a degradation of spatial resolution and sensitivity to equilibrium-type segregation, where the width of the segregant layer is less than that of the electron probe trying to determine its extent.

Under ideal conditions the thinnest areas of the foil will lead to the best resolution and sensitivity for analysis; in reality, counting times, surface artefacts and background radiation (for active foils) become dominant factors. For very thin specimens the X-ray generation rate is low and data acquisition must be performed for longer times to improve counting statistics. Apart from the inconvenience of slower analysis, longer counting times also give more opportunity for specimen drift.

Surface films are present on most real specimens, arising from the preparation route and storage. These films are of approximately constant thickness which clearly becomes a greater proportion of the total specimen thickness as the foil thickness diminishes. For the thin foils in this study, chlorine from the perchloric acid polishing solution was found to be present as a surface artefact; its presence being more obvious in X-ray spectra obtained from thinner sections.

A related effect of a constant background 'noise' peculiar to the active material is the X-ray count generated by the specimen's induced radioactivity. This is dealt with further in relation to spectrum quantification, but its magnitude is constant and thus its effect is clearly proportionately greater the lower the rate of electron beam X-ray generation.
Thus the optimum specimen thickness is a compromise, so that the electron generated X-ray count is as high as possible without significant beam broadening occurring. With experience it was found that choice of suitable foil thicknesses became largely intuitive. Some measurements were made of local foil thickness by EELS or scaling integrated counts through and adjacent to voids of measured diameter. The thicknesses measured were less than 50 nm, with 40 nm being typical.

3.6.3.4 Boundary tilt

Owing to the fine electron probe employed in this work, boundary misorientation is also of particular importance to microanalytical resolution. For a larger probe size of, say, 15 to 20 nm, as with thermionic sourced instruments, substantial boundary orientation misalignment would be required for the boundary to fall outside the analysed volume through the thickness of the foil. A simple calculation of electron probe / boundary geometry reveals that misorientations of greater than 11° for a 20 nm diameter probe, but only 1.1° for a 3 nm diameter probe, are necessary for part of the boundary plane to lie outside the analysed volume. (This calculation assumes a foil thickness of 50 nm, a planar boundary of width 2 nm centred under the incident probe and neglects beam broadening effects).

Vatter and Titchmarsh [196] and Titchmarsh [197] have performed Monte-Carlo calculations to predict the influence of boundary misorientation on measured EDX compositional profiles. Figure 3.7(a) shows the variation in phosphorus concentration detected at the boundary plane as a function of boundary tilt, whilst Figure 3.7(b) illustrates the predicted effect of misorientation on the shape of a derived concentration profile across an interface.

3.6.4 Spectrum quantification

There are essentially two stages to the quantification of generated X-ray spectra: spectrum treatment to extract elemental peak intensities and then conversion of these intensities to yield elemental concentrations. The first stage involves the removal of escape peaks, deconvolution of overlapping peaks and fitting reference peak shapes to the filtered spectrum. The second stage ratios the raw elemental peak intensities to a single element and may correct for any absorption.

For this work the Link Analytical quantification package RTS2/FLS (Ratio Thin Section, Filtered Least Squares) was used with the AN10000 microanalysis system to carry out the first stage for all spectra acquired. The element list used to fit the spectra to always consisted of at least the elements Fe, Cr, Ni, Si, Mn, Mo, V, Nb and P. Further
Figure 3.7: Effect of boundary tilt on (a) the calculated and experimental phosphorus concentrations determined at boundary planes in a 2.25Mo-1Cr steel [196] and (b) the theoretical concentration profile of a 25% monolayer phosphorus segregation in iron [195].
elements were added if their presence was indicated by unaccounted for peaks in the X-ray spectrum. The spectra were refitted with a modified element list or different gain calibration spectrum if the reported 'Fit Index' was significantly greater than the statistically ideal value of 1 until the fit was improved.

For spectra obtained from inactive foils, the RTS2/FLS package was also used to perform the second stage of the analysis to provide normalized quantitative compositional data. The method is the familiar one of ratioing the characteristic intensities to that of, in this case, silicon by Cliff-Lorimer factors [198] to provide mass composition ratios. Absorption corrections were not applied.

Spectra obtained from active foils had to be corrected for their intrinsic 'spectra' arising from the induced radioactivity of the specimen. An example of such a spectrum, obtained by counting in the absence of electron beam excitation, is shown in Figure 3.8(a). This spectrum was obtained from a reduced activity composite thin foil, yet a significant number of X-ray counts are still detected; as noted above, conventional 3 mm diameter thin foils of irradiated material caused complete saturation of the X-ray detector, with a reported count rate in excess of 30 000 cps. The major peak in the 'no-beam' spectrum corresponds to that of Mn Kα with its accompanying Kβ. The capture of an extra neutron by 54Fe forms the unstable 55Fe nuclide. This decays by electron capture to 55Mn, whereby a K-shell electron combines with a proton in the unstable nucleus forming a neutron via the reaction:

\[ p + e \rightarrow n + \gamma \]

The resulting hole in the K-shell is filled by electronic transition with the simultaneous generation of characteristic Mn K-line X-rays. These in turn fluoresce the high concentration of chromium present in the steel to generate Cr K-line X-rays. Furthermore there is an increase in the low energy background levels which makes quantification of elements with characteristic X-ray energies in this region more subject to error. This 'no-beam' spectrum will be superimposed on any electron beam generated X-ray spectrum collected, to give a composite spectrum as shown in Figure 3.8(b).

To correct for this, a 'no-beam count' spectrum was collected after acquiring each series of spectra across every interface analysed, thus compensating for specimen-detector geometrical variations. A straightforward subtraction of this 'no-beam count' from each spectrum obtained in a profile proved unsuitable, since the Mn Kα peak intensity was often actually greater in the 'no-beam count' than in the electron beam generated spectrum; presumably this arises from counting errors stemming from the relatively high
Figure 3.8: Typical X-ray spectra obtained from neutron irradiated FV448 thin foils; (a) 'No-beam count', collected from the induced activity of the irradiated material in the absence of electron beam excitation, (b) Electron beam generated spectrum with superimposed 'no-beam count'.
dead times of 45%. The result is that individual channels are then assigned a negative intensity, which causes failure of the RTS2 quantification routine. Instead, the 'no-beam count' spectrum was scaled via the integrated manganese peak intensity to each generated spectrum. The scaled peak intensities of iron and chromium were then subtracted from the generated spectra to give corrected elemental peak intensities. These corrected elemental peak areas were then ratioed in the standard way by their relevant KxSi 'Cliff-Lorimer' factors to give normalized elemental concentrations.

3.7 Elemental mapping

Construction of spatial compositional profiles from the off-normal weld suggested an inhomogeneous solute distribution on a larger scale than boundary effects. To investigate this inhomogeneity and to try to correlate it with the microstructure, the HB501 was used to perform digital mapping. The Link Analytical AN10000 microanalysis system is equipped with an ADM (Acquire Digital Map) software package. The FEGSTEM electron probe is driven across the specimen in a grid pattern by the AN10000, providing the automatic simultaneous acquisition of up to 18 images. Data for the images is collected from specified energy 'windows' defined in the X-ray spectrum corresponding to elements of interest, and from the bright field detector to form a digitized bright field image.

Image resolution is variable from 32 x 32 to a maximum array of 512 x 512 image points. The latter corresponds to approximately 3.5 nm per pixel at a magnification of 50 000 x. The useful image information is also dependent upon the dwell time per pixel. Ideally, as long a time as possible is desirable. However, the long term stability of the FEG source limits the total analysis time to about 1 hour if a tip excursion is not to cause a sudden significant fall in probe current, and hence count rate. Thus for a 512 x 512 pixel image a 10 ms dwell time per image point was the maximum that could be used to be reasonably confident of providing a constant probe current over the scanned area. Specimen drift considerations place a limit on the maximum magnification to be used at 100 000 x, before image shearing becomes recognizable, without an automated drift corrected mapping facility.

The dwell time per pixel was only tens of milliseconds, thus the total number of X-ray counts per pixel was correspondingly low, and for discrete elemental energy windows lower still. Since the ultimate spatial resolution was not so critical at these lower magnifications a VOA of twice the diameter was used to increase the probe current by a factor of four over that used for the high resolution interfacial profiling. This generated
X-ray counts of about 5000 cps, necessitating a change of pulse processor time to reduce the processor dead time.

The acquired X-ray energy maps and electron images are written direct to disc, from where they may be accessed for subsequent manipulation within the DIGIPAD image processing software package.

### 3.8 Bulk examination of weld zone material

A piece of unirradiated weld zone material was sectioned across the weld line to provide a specimen approximately 20 × 10 × 3 mm. This was incorporated into a 38 mm diameter bakelite mount, wet ground on silicon carbide papers and polished to a 1/4 µm diamond paste finish. Etching was carried out using Vilellas Reagent to clearly reveal the fusion and heat affected zone boundaries. Examination was performed firstly using a Reichart-Jung MeF₃ optical microscope to characterize the microstructure across the weld line.

The specimen was further examined with the aid of a Cambridge Instruments Stereoscan 360 scanning electron microscope to provide information on the variation in chemical composition across the whole weld. This microscope was also interfaced to a Link Analytical AN10000 microanalysis system. The SPECTA software package enables, amongst other things, the specimen stage to be driven between pre-set start and end points, halting at specified intervals under the electron beam to collect X-ray spectra. This procedure was used to generate a compositional linescan across the weld axis. The extremes of the scan were positioned in the parent plate material either side of the axis. X-ray spectra were collected every 250 µm, counting for 100 seconds at each point. The spectra were quantified using the Link Analytical ZAF-4/FLS routine. Atomic number, absorption and fluorescence corrections were applied to apparent concentrations to yield final normalized elemental compositions.
CHAPTER FOUR

Results

4.1 Parent plate

4.1.1 Microstructure

4.1.1.1 As-tempered condition

The general microstructure of the as-tempered FV448 12%CrMoVNi martensitic steel is shown in Figure 4.1. Essentially the microstructure comprised packets of heavily dislocated lath martensite contained within a prior austenite grain boundary (PAGB) network. Irregularly shaped $M_{23}C_6$ precipitates were located principally at prior austenite grain boundaries, but also at lath boundaries and intragranularly. The $M_{23}C_6$ particles were identified by FEGSTEM EDX analysis to have the approximate composition (wt.%) $29\text{Fe}-63\text{Cr}-0.5\text{Ni}-0.3\text{Si}-1.0\text{V}-6\text{Mo}-0.8\text{Mn}$. Additionally, spherical intragranular particles of NbC were also identified.

4.1.1.2 Aged condition

The general microstructure of the parent plate material after ageing at $465^\circ\text{C}$ for 6336 hours is shown in Figure 4.2. There was little modification to the as-tempered lath structure after ageing at this temperature, nor indeed at the lower temperature of $400^\circ\text{C}$. Little change was found in the intragranular precipitation behaviour, but there was evidence of a slight increase in coverage of boundaries by $M_{23}C_6$ precipitation, more particularly following ageing at $465^\circ\text{C}$. The average composition of $M_{23}C_6$ was determined by FEGSTEM EDX as (wt.%): $31\text{Fe}-59\text{Cr}-0.4\text{Ni}-0.3\text{Si}-0.4\text{V}-8\text{Mo}-2\text{Mn}$. Laves phase was not observed in the specimens aged at either 400 or $465^\circ\text{C}$.

4.1.1.3 Irradiated condition

Significant microstructural changes occurred during fast-neutron irradiation at $400^\circ\text{C}$. There was a distinct lowering of dislocation density, but the lath structure was retained, as shown in Figure 4.3. There were several changes to the precipitate population. Firstly, the number of the large (100-200 nm) inter- and intragranular particles was markedly increased following irradiation. Prior austenite grain boundaries in particular became very heavily decorated, having few precipitate-free sections suitable for compositional analysis. This precipitate population included not only the chromium rich $M_{23}C_6$ of the as-tempered and aged conditions, but also a new phase rich in nickel and silicon, as well as chromium-rich relative to the matrix, but not so chromium-rich as $M_{23}C_6$. The composition of this new phase as determined by FEGSTEM EDX analysis
Figure 4.1: General microstructure of FV448 parent plate material in the as-tempered condition.
Figure 4.2: General microstructure of FV448 parent plate material aged at 465°C for 6336 hours.
Figure 4.3: General microstructure of FV448 parent plate material fast neutron irradiated at 400°C to a damage level of 33 dpa(NRT).
types of precipitate were immediately distinguishable by the appearance of large characteristic nickel and silicon X-ray peaks in the spectra generated from the new phase, but almost absent in spectra from $\text{M}_{\text{23}}\text{C}_6$ particles, as shown in Figures 4.4 and 4.5. Furthermore, the particles of $\text{M}_{\text{23}}\text{C}_6$ were often seen to be internally damaged following irradiation, whereas particles of the new phase were not, illustrated in Figure 4.6. Grain boundary coverage consisted of a higher proportion of $\text{M}_{\text{23}}\text{C}_6$; the irradiation-induced phase was more prevalent intragranularly and was often found to be nucleated on pre-existing irradiation damaged $\text{M}_{\text{23}}\text{C}_6$ particles.

Additionally a very finely dispersed intragranular precipitate phase, typically 20 nm in diameter, was observed in material irradiated at 400°C. This phase was distributed heterogeneously throughout the matrix, tending to form in regions where the larger nickel- and silicon-rich phase, described above, was relatively absent. The composition of this finer phase was also very rich in nickel and silicon, whilst chromium was virtually absent, as indicated by the X-ray spectrum in Figure 4.7. The apparent typical composition when analysed through the foil thickness by FEGSTEM EDX was (wt.%) 21Fe-2Cr-50Ni-13Si-0.5V-0.4Nb-0.8Mo-2P-11Mn. Since these particles are smaller in diameter than the typical foil thickness, there will be a contribution to their apparent composition from the surrounding matrix material. The apparent concentrations of iron and chromium detected are in direct proportion to their matrix concentrations. Assuming that all the chromium X-ray signal, and thus the proportionate iron signal, comes from the matrix yields a composition corrected for the matrix contribution of about (wt.%) 65Ni-17Si-14Mn-0.6V-0.5Nb-1Mo-2.5P.

Neutron irradiation at 465°C caused a further reduction in dislocation density, coupled with well defined polygonization and subgrain formation as can be seen in Figure 4.8. The precipitate phases observed were the same as for the lower temperature irradiation, but with slight modifications in relative distribution. The prior austenite and lath boundary precipitation was very similar to that produced after neutron irradiation at 400°C. A mixed population of chromium-rich (25Fe-66Cr-1Ni-0.7Si-0.4V-7Mo-0.4Mn) and nickel and silicon enriched (19Fe-35Cr-21Ni-9Si-1.5V-1Nb-10Mo-2.5Mn-1P) precipitates were detected, with relatively more of the latter phase present than following the lower temperature irradiation.

The very fine intragranular phase observed after irradiation at 400°C was far less evident following neutron irradiation at 465°C, coincident with an increase in the population of the larger nickel- and silicon-rich phase described above. Occasional regions of intragranular precipitates 20-30 nm in diameter were observed and their apparent
Figure 4.4: Typical X-ray spectrum obtained from M_{23}C_6 precipitate in neutron irradiated FV448, with contribution from 'no-beam count' stripped out.

Figure 4.5: Typical X-ray spectrum (corrected for 'no-beam count') obtained from the large radiation-induced precipitate phase observed in irradiated FV448, showing it to be enriched in nickel and silicon.
Figure 4.6: Mixed population of internally damaged $\text{M}_2\text{C}_6$ particles (arrowed A) and precipitate phase enriched in nickel and silicon (arrowed B) in FV448 parent plate material irradiated to 33 dpa(NRT) at 400°C.
Figure 4.7: Typical X-ray spectrum (corrected for 'no-beam count') obtained from the finely dispersed radiation-induced phase observed in irradiated FV448, showing it to be highly enriched in nickel and silicon.
Figure 4.8: General microstructure of FV448 parent plate material fast neutron irradiated at 465°C to a damage level of 50 dpa(NRT).
composition determined as (wt.%): 9Fe-1.5Cr-22Ni-15Si-3Nb-3Mo-1.5P-14Mn. Again, after correcting for an estimated matrix contribution to the analysed X-ray signal, their mean composition was about (wt.%): 60Ni-17Si-3.5Nb-3Mo-1.5P-15Mn.

Direct evidence for displacement damage arising from irradiation was provided by the presence of dislocation loops and, to a lesser extent, the formation of a sparsely distributed population of voids. Detailed analysis of dislocation loop geometries and distributions in neutron irradiated FV448 steel has been previously published [191]. Thus it was felt unnecessary to carry out a further detailed investigation of loop geometry in this steel under almost identical irradiation conditions. However, a brief examination was performed, with a typical dislocation structure for material irradiated at 465°C as shown in Figure 4.9. The foil orientation relative to the beam direction was close to [001], with the [011] operating reflection. Several rectilinear loops are visible with edges aligned in the projected (100) directions, such as marked A. Additionally traces of loops aligned edge-on, such as marked B, were visible. With the foil tilted so that the beam direction was approximately parallel to [111] the dislocation loops appeared lozenge-shaped, as shown in Figure 4.10. In the centre of the micrograph, using the [110] operating reflection, can be seen the projection of an arrangement of three such loops marked at A, as well as other individual loops. The loops are quite large, for example the projected dimensions of the three loops at A in Figure 4.10 being 30-50 nm across. As such, it would be expected that loops lying out of the plane of the foil would not be wholly contained by the thin foil. Thus some of the dislocation lines imaged are probably segments of dislocation loops lying out of the plane of the foil.

Further evidence of radiation damage was the existence of occasional very small voids in the irradiated microstructure. The voids were not actually visible looking at the live image on the phosphor screen of the TEM. They only became evident upon close examination of high magnification micrographs of very thin regions of foil where kinematical contrast conditions were operating, emphasizing mass thickness variations. Figure 4.11 shows a region from a thin foil of material irradiated at 465°C. Just visible are three voids (arrowed) approximately 5 nm in diameter. It should be emphasized that voids were seldom observed in the irradiated parent plate material at either irradiation temperature. In fact this micrograph was the only region found to contain more than one void in the image and thus represents the area observed with maximum voidage - certainly not a typical region.
Figure 4.9: Dislocation structure in FV448 parent plate irradiated to 50 dpa(NRT) at 465°C. Foil oriented to near [001]: rectilinear loops perpendicular to incident beam marked A, loops aligned edge-on to beam direction marked B.
Figure 4.10: Dislocation structure in FV448 parent plate irradiated to 50 dpa(NRT) at 465°C. Foil oriented to near [111]; array of three dislocation loops marked at A.
Figure 4.11: Fine-scale microstructure of FV448 parent plate material irradiated to 50 dpa(NRT) at 465°C. Three voids just resolvable are arrowed.
4.1.2 Interface microchemistry

4.1.2.1 As-tempered condition

Microchemical profiles, shown as a function of distance from prior austenite grain boundaries and lath boundaries in Figures 4.12 and 4.13 respectively, were constructed for the elements Fe, Cr, Ni, Si, Mn, Mo and P. The profiles represent the mean concentration (wt.%) of each element from five analyses across either side of the relevant interface. The error bars associated with each data point correspond to the standard error \( \frac{\sigma}{\sqrt{n}} \) for each calculated mean elemental concentration, where \( \sigma \) is the standard deviation of the data points and \( n \) their number.

When quantifying the collected spectra, peak areas for niobium and vanadium were also fitted but concentration profiles were not constructed for them. In the case of niobium the errors associated with fitting the Nb L-peak in the low energy end of the spectrum were large since it was overlapped by the Mo L- and P K-peaks, as well as having a relatively large contribution from the continuous Bremsstrahlung radiation. As such, the fitting error was usually of the same order as the peak area itself. This, coupled with the large scatter in the derived concentrations (often being 'negative' concentrations) led to the absence of meaningful results. The V K-peak is sufficiently isolated from other detected peaks in this alloy to be accurately fitted without other peaks overlapping. However, the very low concentration of vanadium in this alloy, at 0.14 wt.%, also meant that the fitted peak area was invariably less than the fitting error. Moreover, no significant change in the concentration of vanadium at boundaries was apparent for any material condition. Similar arguments also apply to the detection and peak fitting of molybdenum and phosphorus and indeed large errors were also associated with their respective derived concentrations. However, significant changes in boundary concentration of these elements were detected for most material conditions, hence the inclusion of their concentration profiles.

From the spatial compositional profiles of Figure 4.12 it can be seen that there is in fact evidence of non-uniform composition across prior austenite grain boundaries even in the as-tempered condition. Chromium, molybdenum, phosphorus and, to a lesser extent, manganese were found to be located preferentially at these boundaries. The apparent width of the enriched region, as detected, extended to less than 5 nm either side of the boundary plane. In contrast, the concentrations of nickel and silicon were observed to be uniform across prior austenite boundaries. The iron concentration simply reflects the net solute redistribution and was thus found to be depleted at prior austenite grain boundaries.
Figure 4.12: The variation of mean solute concentration as a function of distance from prior austenite grain boundary planes in as-tempered FV448.
Figure 4.13: The variation of mean solute concentration as a function of distance from lath boundary planes in as-tempered FV448.
Turning to the corresponding lath boundary profiles for the as-tempered condition it is clear that the spatial distributions of solute concentration are much more uniform than those across prior austenite grain boundaries. There is the slightest indication that the boundary plane concentration of molybdenum is increased, but there is some scatter and thus relatively large associated standard errors.

4.1.2.2 Aged condition

Figure 4.14 illustrates the mean elemental concentration profiles obtained across either side of five prior austenite grain boundaries after ageing at 400°C for 6840 hours. Clearly there is grain boundary enrichment of all solutes and a consequent depletion of iron. (Note that there is a significant change of scales for molybdenum and phosphorus compared with the previous Figures 4.12 and 4.13). Figure 4.15 shows the corresponding mean concentration profiles determined across five lath boundaries for the same material condition. Similarly, results for five prior austenite and lath boundaries from material aged at 465°C for 6336 hours are summarized in Figures 4.16 and 4.17 respectively.

It is apparent that, in general, grain boundary solute enrichment was found to be greatest at prior austenite grain boundaries after ageing at the higher temperature of 465°C. The solute specific effects of boundary type and ageing temperature on boundary composition are shown more clearly in Figures 4.18 to 4.23 for individual element mean concentration profiles.

Turning firstly to the major solute of chromium, Figure 4.18, it is clear that both boundary types become enriched in chromium after ageing at either temperature. Ageing at 400°C resulted in the measured mean boundary concentration at both boundary types being almost identical. The rise, however, is more significant for lath boundaries in comparison to the as-tempered material, where lath boundaries failed to show any enrichment, whilst there was a detectable increase in prior austenite grain boundary chromium concentration even in the as-tempered condition. Ageing at 465°C caused a substantial increase in boundary chromium concentration at both lath boundaries and, to a greater extent, at prior austenite grain boundaries. The widths of the segregated layers, as measured by their full width half maxima (FWHM), are given in Table 10: in each case they were less than 5 nm.

Nickel was found to be consistently enriched at lath and prior austenite grain boundaries after ageing at 400 and 465°C, as shown in Figure 4.19. A slight variation with ageing temperature was detected, with the boundary concentration being greater following
Figure 4.14: The variation of mean solute concentration as a function of distance from prior austenite grain boundary planes in FV448 aged for 6840 hours at 400°C.
Figure 4.15: The variation of mean solute concentration as a function of distance from lath boundary planes in FV448 aged for 6840 hours at 400°C.
Figure 4.16: The variation of mean solute concentration as a function of distance from prior austenite grain boundary planes in FV448 aged for 6336 hours at 465°C.
Figure 4.17: The variation of mean solute concentration as a function of distance from lath boundary planes in FV448 aged for 6336 hours at 465°C.
Figure 4.18: Mean solute concentration as a function of distance from boundary type in FV448 aged at 400°C and 465°C.
Figure 4.19: Mean solute concentration as a function of distance from boundary type in FV448 aged at 400°C and 465°C.
Figure 4.20: Mean solute concentration as a function of distance from boundary type in FV448 aged at 400°C and 465°C.
Figure 4.21: Mean solute concentration as a function of distance from boundary type in FV448 aged at 400° and 465°C.
Figure 4.22: Mean solute concentration as a function of distance from boundary type in FV448 aged at 400°C and 465°C.
PHOSPHORUS

Figure 4.23: Mean solute concentration as a function of distance from boundary type in FV448 aged at 400°C and 465°C.
Table 10

Full width half-maxima values of interfacial solute segregant layer widths in aged FV448.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Segregant width, FWHM (nm)</th>
<th>400 °C ageing</th>
<th></th>
<th>465 °C ageing</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PAGB</td>
<td>Lath b.</td>
<td>PAGB</td>
<td>Lath b.</td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
<td>2.9</td>
<td>3.3</td>
<td>4.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td>3.8</td>
<td>3.3</td>
<td>3.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Silicon</td>
<td></td>
<td>4.8</td>
<td>2.8</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Manganese</td>
<td></td>
<td>3.3</td>
<td>3.8</td>
<td>3.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td></td>
<td>3.3</td>
<td>3.5</td>
<td>3.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Phosphorus</td>
<td></td>
<td>3.3</td>
<td>3.3</td>
<td>3.9</td>
<td>3.3</td>
</tr>
</tbody>
</table>
ageing at 400°C for both lath and prior austenite grain boundaries. The dominant factor in boundary nickel concentration was found to be boundary type: prior austenite grain boundaries aged at both temperatures became higher in nickel concentration than lath boundaries aged at either temperature. Again, the segregated layer widths, as defined by the full width half maxima, are given in Table 10 and were each less than 5 nm.

The profiles for silicon in Figure 4.20 show lath boundaries and prior austenite grain boundaries to become slightly enriched in silicon to a very similar extent following ageing at 400°C. Ageing at 465°C caused lath boundaries to show an almost identical slight enrichment. However, ageing at 465°C caused the prior austenite grain boundary concentration of silicon to show a considerable increase. Table 10 lists the segregated region widths of each profile, determined by the full width half maxima.

Figure 4.21 illustrates the detected manganese concentration as a function of distance from the interface, varying with boundary type and ageing temperature. The dominant factor was boundary type: prior austenite boundaries in material aged at both temperatures exhibited greater enrichments of manganese than did lath boundaries aged at either temperature. For both boundary types greater solute enrichment was seen after ageing at 465°C rather than 400°C. The full width half maxima of the segregated zones are in each case less than 4 nm, as given in Table 10.

It was molybdenum of all the solutes which showed the greatest absolute change in boundary concentration during thermal ageing, as illustrated by Figure 4.22. The dominant factor was ageing temperature: far higher concentrations of molybdenum were recorded at either boundary type following ageing at 465°C than were found at both boundary types after ageing at 400°C. Again the prior austenite grain boundaries exhibited greater solute enrichment than did the lath boundaries at each ageing temperature. Despite the huge prior austenite grain boundary concentrations of molybdenum detected in the material aged at 465°C, at some boundaries exceeding 20 wt.%, the full width half maxima of the segregated zones were still only approximately 3 nm, Table 10.

Whilst molybdenum exhibited the greatest absolute increase in boundary concentration it was phosphorus which showed the greatest relative increase in concentration at boundaries, Figure 4.23. Phosphorus is present only as an impurity in FV448, at a concentration of approximately 0.006 wt.% in the bulk; yet in the boundary volumes analysed it was detected to be present in concentrations exceeding 2 wt.% at some prior austenite grain boundaries from material aged at 465°C. The relative effects of ageing temperature and boundary type on phosphorus boundary concentration are the same as
for chromium and molybdenum. Again, ageing temperature rather than boundary type was the dominant factor, with ageing at 465°C prompting substantially higher phosphorus concentrations at both boundary types than ageing at 400°C did at either type. For each ageing temperature prior austenite grain boundaries became more segregated than did lath boundaries. Again, Table 10, the segregated layer widths measured by their full width half maxima were less than 4 nm.

4.1.2.3 Irradiated condition

The mean solute concentration profiles determined across prior austenite grain boundaries and lath boundaries from parent plate material neutron irradiated at 400 and 465°C are shown in Figures 4.24 to 4.27. Data for the same elements as for the as-tempered and aged material are plotted. It should be noted for manganese, however, that owing to the method used for spectrum correction and quantification that the absolute scale may be in error by a certain factor for each profile. Thus comparison of absolute values of manganese concentrations between different profiles must be treated with caution. Nevertheless, the trends of the variation in manganese concentration with distance from the interfaces ought to be valid. As with data from the aged material, comparison of the twin effects of irradiation temperature and boundary type is facilitated by plotting the mean profiles for each material condition on single graphs for individual solutes, as performed in Figures 4.28 to 4.33.

Dealing firstly with chromium - the major solute - the mean solute concentration profiles in Figure 4.28 show the boundary concentration to be locally higher than the immediately adjacent matrix concentration. However, there is a distinct reduction in matrix chromium concentration towards the boundary. This depletion was found to be most marked at prior austenite grain boundaries following irradiation at 400°C, but with no rational dependence upon irradiation temperature or boundary type. In contrast, the effects of irradiation temperature and boundary type on the localized increase in boundary concentration of chromium could be rationalized. The dominant factor was found to be boundary type with prior austenite grain boundaries exhibiting greater local enrichment than lath boundaries. For each particular boundary type the higher irradiation temperature of 465°C was found to cause a greater local enrichment than the lower irradiation temperature, 400°C. Table 11 lists the full width half maxima measures of enriched layer width, each being less than 4 nm.

Figure 4.29 shows the corresponding mean concentration profiles for nickel across boundaries in irradiated material. Boundary enrichment of nickel for all material conditions is apparent. The detected boundary concentrations were found to be similar
Figure 4.24: The variation of mean solute concentration as a function of distance from prior austenite grain boundary planes in FV448 fast neutron irradiated to 33 dpa at 400°C.
Figure 4.25: The variation of mean solute concentration as a function of distance from lath boundary planes in FV448 fast neutron irradiated to 33 dpa at 400°C.
Figure 4.26: The variation of mean solute concentration as a function of distance from prior austenite grain boundary planes in FV448 fast neutron irradiated to 50 dpa at 465°C.
Figure 4.27: The variation of mean solute concentration as a function of distance from lath boundary planes in FV448 fast neutron irradiated to 50 dpa at 465°C.
Figure 4.28: Mean solute concentration as a function of distance from boundary type in FV448 irradiated at 400°C and 465°C.
Figure 4.29: Mean solute concentration as a function of distance from boundary type in FV448 irradiated at 400°C and 465°C.
Figure 4.30: Mean solute concentration as a function of distance from boundary type in FV448 irradiated at 400°C and 465°C.
Figure 4.31: Mean solute concentration as a function of distance from boundary type in FV448 irradiated at 400°C and 465°C.
Figure 4.32: Mean solute concentration as a function of distance from boundary type in FV448 irradiated at 400°C and 465°C.
Figure 4.33: Mean solute concentration as a function of distance from boundary type in FV448 irradiated at 400°C and 465°C.
Table 11

Full width half-maxima values of interfacial solute segregant layer widths in irradiated FV448.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Segregant width, FWHM (nm)</th>
<th>400°C irradiation</th>
<th>465 °C irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PAGB</td>
<td>Lath b.</td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
<td>3.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td>3.8</td>
<td>4.3</td>
</tr>
<tr>
<td>Silicon</td>
<td></td>
<td>4.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Manganese</td>
<td></td>
<td>3.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Molybdenum</td>
<td></td>
<td>4.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Phosphorus</td>
<td></td>
<td>4.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>
for each condition, but the irradiation temperature proved to cause a greater effect than boundary type; the detected boundary nickel concentration was slightly higher at boundaries from material irradiated at 465°C. The differences between boundary type caused only minor variations in detected boundary nickel concentration, with prior austenite grain boundaries being slightly more enriched than lath boundaries. Following neutron irradiation at 400°C the matrix nickel concentrations was consistently, but marginally, lower than that in material irradiated at 465°C. The segregated layer widths of the profiles for each material condition were around 4nm, Table 11.

Mean concentration profiles for silicon across boundaries in irradiated FV448 are shown in Figure 4.30. Solute enrichment was detected at each boundary type for both irradiation temperatures. The irradiation temperature was the dominant factor in determining boundary enrichment. Significantly higher silicon concentrations were recorded at boundaries after 400°C neutron irradiation than following irradiation at 465°C. Of the boundary types, prior austenite grain boundaries exhibited greater enrichment than did lath boundaries at both irradiation temperatures. In common with the nickel profiles above, the matrix concentration of silicon was found to be consistently, albeit marginally, lower in material irradiated at 400°C compared with that irradiated at 465°C. Again, 3-4 nm was found to be the typical segregated layer width, Table 11.

As noted above, the absolute values for manganese concentration cannot necessarily be relied upon to allow quantitative comparison of magnitudes between profiles. However, it is clear from Figure 4.31 that the boundary composition became enhanced in manganese relative to the immediately adjacent matrix material following irradiation at both temperatures. The indication from the profile set, with the above reservations, is that boundary type appears to play a more important role in the degree of solute enrichment. Prior austenite grain boundaries were markedly higher in manganese concentration than lath boundaries. As for the effect of irradiation temperature, it was found that irradiation at 465°C prompted slightly greater enrichment of manganese at the interfaces than 400°C irradiation.

The mean concentration profiles from irradiated material for molybdenum and phosphorus show similar trends, Figures 4.32 and 4.33 respectively. The dominant factor governing the extent of solute enrichment is the boundary type for both solutes. Prior austenite grain boundaries exhibited considerably greater concentrations of each solute than lath boundaries at either irradiation temperature. The effect of irradiation temperature was also the same for both solutes; more solute enrichment at boundaries was detected in material irradiated at 465°C than material irradiated at 400°C. So too are the widths of segregated layers for each material condition similar, as listed in Table 11.
4.1.2.4 Comparison of as-tempered, aged and irradiated interfacial microchemistry

An indication of how the relative boundary plane solute concentrations are affected by thermal and irradiation treatment temperatures and boundary type can be gained from Table 12. For each solute, the profiles according to boundary type and treatment temperature are listed in descending order of solute enrichment. For the aged material, in general, the treatment temperature seems to be the dominant factor, with greater solute enrichment at both boundary types at the higher temperature than at either boundary type at the lower temperature. In the irradiated material the dominant factor seems to be the boundary type; greater solute enrichment was found at prior austenite grain boundaries at both irradiation temperatures than at lath boundaries at either temperature.

Comparison of the solute concentration profiles obtained from irradiated material with those obtained from material in the as-tempered condition indicates the gross effect of the irradiation history on the starting material. However, the net effect of neutron irradiation on boundary region microchemistry is revealed only when the relevant solute distribution profiles are compared with those from the corresponding aged material to discount the purely thermal effects of the irradiation history.

The concentration profiles obtained for chromium from as-tempered, aged and irradiated material are plotted for each of the four combinations of boundary type and temperature in Figures 4.34 to 4.37. Several points emerge. Firstly, although each of the irradiated boundary planes were locally enriched relative to the adjacent matrix, the detected boundary concentrations from the irradiated material were actually only equal to or just less than the corresponding mean boundary concentrations from the as-tempered material. The matrix chromium concentrations near to, but not at, the boundary plane are markedly reduced from the as-tempered condition following irradiation at both temperatures. This reduction increases with decreasing distance from the boundary plane, until at the boundary plane itself there is an upturn in the chromium concentration in the irradiated material. Thus there is a minimum in apparent chromium concentration at between 5 and 10 nm from the boundary plane, corresponding to a depletion of 1.5 to 2 wt.% from values detected in the as-tempered material. These then are the gross effects of irradiation; the combined effects of prolonged thermal treatment and a fast neutron flux. If now the chromium concentration profiles from the irradiated material are compared with those obtained from aged material in Figures 4.34 to 4.37, the solute redistribution arising solely from the effect of the neutron flux can be gauged. A straight subtraction of the respective aged material concentration profiles from the irradiated material concentration profiles are shown in Figure 4.38, to give an apparent net irradiation effect.
Table 12

Summary of relative effect of treatment temperature and boundary type on mean boundary plane solute concentration in aged and irradiated parent plate FV448.

<table>
<thead>
<tr>
<th></th>
<th>Treatment</th>
<th>Chromium</th>
<th>Nickel</th>
<th>Silicon</th>
<th>Manganese</th>
<th>Molybdenum</th>
<th>Phosphorus</th>
</tr>
</thead>
</table>

where 465/PAGB denotes prior austenite grain boundaries at 465°C etc.
Figure 4.34: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 400°C.
Figure 4.35: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 400°C.
Figure 4.36: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 465°C.
Figure 4.37: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 465°C.
Figure 4.38: Net effect of irradiation on solute concentration as a function of distance from boundary planes in FV448.
on solute redistribution. From this it can be seen that despite the upturn in gross chromium concentration at boundary planes in irradiated material to near as-tempered values, the net irradiation effect is actually one of chromium depletion from boundaries apparently extending to the boundary plane itself.

Comparing now the solute concentration profiles for nickel from as-tempered and irradiated material for each of the four combinations of boundary type and temperature as illustrated in Figures 4.39 to 4.42. It is immediately clear that elevated temperature neutron irradiation prompts a significant reduction of nickel concentration in the matrix remote from boundaries, from an initial 0.6 wt.% to about 0.25 wt.% and 0.15 wt.% following irradiation at 465 and 400°C respectively. For each of the four boundary / temperature permutations, prolonged irradiation at temperature also caused a marked increase in boundary nickel concentration - not just relative to the adjacent depleted matrix, but to values above those of as-tempered material. Comparison with the concentration profiles from the aged material shows that there is a similar increase in boundary plane nickel concentration, but that there is no reduction in matrix concentration following thermal ageing. Performing a straight subtraction of the aged material concentration profiles to give the apparent net irradiation effect yields the results shown in Figure 4.43. The major net irradiation effect is to reduce the matrix nickel concentration; the effect being greater following the lower temperature irradiation at 400°C. The apparent net effect of irradiation on the nickel concentration at the boundary plane is more complex. At prior austenite grain boundaries there is little deviation from the general matrix reduction of nickel concentration at either irradiation temperature. At lath boundaries, however, the general reduction in matrix nickel concentration is not followed. Instead there is a net rise in apparent nickel concentration at lath boundaries relative to the adjacent matrix. This rise is such that at lath boundaries in material irradiated at 465°C there was actually a detected net increase in nickel concentration relative to lath boundaries in material aged at the same temperature.

The effects of neutron irradiation on the mean concentration profiles obtained for silicon are broadly similar to those for nickel, in that there is a distinct reduction in matrix concentration of both solutes remote from boundary planes, Figures 4.44 to 4.47. The matrix concentration of silicon in the as-tempered material was found to be 0.6 wt.%, falling to 0.25 wt.% in material irradiated at 400°C and to 0.35 wt.% in material irradiated at 465°C. There was found to be a real increase in boundary plane silicon concentration over the as-tempered condition for each irradiation temperature / boundary type combination; not simply an increase relative to the adjacent depleted matrix. The enrichment was found to be greater following irradiation at the lower temperature of 400°C. In contrast, ageing at 400°C was found to only slightly increase the concentration
Figure 4.39: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 400°C.
Figure 4.40: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 400°C.
Figure 4.41: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 465°C.
Figure 4.42: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 465°C.
Figure 4.43: Net effect of irradiation on solute concentration as a function of distance from boundary planes in FV448.
Figure 4.44: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 400°C.
Figure 4.45: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 400°C.
Figure 4.46: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 465°C.
Figure 4.47: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 465°C.
Figure 4.48: Net effect of irradiation on solute concentration as a function of distance from boundary planes in FV448.
of silicon detected at boundaries, whilst ageing at 465°C produced greater enrichment. Ageing was found not to change the matrix concentration of silicon from the as-tempered values of 0.6 wt.%. Thus the net effect of irradiation on the silicon concentration near to boundaries is shown in Figure 4.48. It is evident from this that irradiation was found to cause a fairly constant reduction in matrix silicon concentration of about 0.3 wt.%. At the boundary planes however, net silicon enrichment was detected at both prior austenite and lath boundaries following 400°C irradiation over and above that produced by equivalent thermal ageing; the net enrichment being greater at the prior austenite grain boundaries.

For reasons detailed previously, the manganese concentration profiles determined from irradiated material may not be quantitatively correct in absolute terms, but the relative spatial values for each profile should be quantitatively valid. Figures 4.49 to 4.53 illustrate the effects of ageing and irradiation on the concentration profiles obtained for manganese. Figure 4.54 attempts to depict the net effect of irradiation on spatial molybdenum concentration. The profiles from irradiated material were normalized to the corresponding profiles from aged material at a distance of 100 nm from the boundary plane by the addition of a constant in each case. Although little quantitative data may be drawn, it is apparent from this analysis that the net effect of irradiation on the manganese distribution is to deplete the solute from boundary regions.

Comparison of the molybdenum concentration profiles obtained from irradiated material with those from as-tempered material, Figures 4.54 to 4.57, show the detected boundary plane concentrations to be very similar for each boundary type / temperature combination. The molybdenum concentrations away from boundaries following irradiation was generally lowered from the as-tempered values. In contrast, ageing caused substantial boundary enrichment with dramatic increases in molybdenum concentration detected at both lath and particularly prior austenite grain boundaries after ageing at 465°C. The net effects of irradiation on molybdenum redistribution are shown in Figure 4.58. The absence from the irradiated material of the substantial molybdenum enrichment seen in the thermal controls at boundary planes is effectively a net depletion - which is thus significantly greater in material irradiated at 465°C.

The relative effects of irradiation and ageing on the mean phosphorus concentration profiles (Figures 4.59 to 4.62) are very similar to those described for molybdenum above. Irradiation was found to cause an increase in boundary phosphorus concentration above as-tempered values. However equivalent thermal ageing produced an even greater boundary enrichment, again particularly at 465°C. Thus the net effect of irradiation,
Figure 4.49: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 400°C.
Figure 4.50: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 400°C.
Figure 4.51: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 465°C.
Figure 4.52: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 465°C.
Figure 4.53: Net effect of irradiation on solute concentration as a function of distance from boundary planes in FV448.
Figure 4.54: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 400°C.
MOLYBDENUM

Figure 4.55: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 400°C.
Figure 4.56: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 465°C.
Figure 4.57: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 465°C.
Figure 4.58: Net effect of irradiation on solute concentration as a function of distance from boundary planes in FV448.
Figure 4.59: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 400°C.
Figure 4.60: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 400°C.
Figure 4.61: Mean solute concentration as a function of distance from prior austenite grain boundaries in FV448 treated at 465°C.
Figure 4.62: Mean solute concentration as a function of distance from lath boundaries in FV448 treated at 465°C.
Figure 4.63: Net effect of irradiation on solute concentration as a function of distance from boundary planes in FV448.
Figure 4.63, was to cause an effective reduction in boundary phosphorus concentration from the values experienced in the thermal control material.

In summary, the apparent net effects of irradiation on interfacial solute concentration were found to be to cause: (i) depletion of chromium, molybdenum, phosphorus (and manganese), (ii) enrichment of nickel at lath boundaries only, at both irradiation temperatures and (iii) enrichment of silicon at 400°C at both boundary types.

4.1.2.5 Post-irradiation annealing

The effects of post-irradiation annealing at 465°C for 1000 hours on the boundary microchemistry of material irradiated at 465°C are shown for each solute discussed above in Figures 4.64 to 4.69.

The major solute, chromium, did appear to exhibit a change in spatial distribution following the annealing treatment, Figure 4.64. There is firstly a rise in boundary chromium concentration detected, more notable at prior austenite grain boundaries, in the annealed specimen. Secondly, the depletion of chromium concentration towards the boundaries found in the irradiated material is much reduced at prior austenite grain boundaries and eliminated at lath boundaries in the annealed material.

Figure 4.65 shows the effect of post-irradiation annealing on solute concentration profiles for nickel at prior austenite and lath boundaries respectively. There is little change in profile shape, but the annealing treatment led to a reduction in apparent nickel concentration at the boundary plane. The reduction was slight in the case of prior austenite grain boundaries, but more pronounced at lath boundaries.

Little change in the corresponding solute concentration profiles for silicon and manganese could be discerned following the post-irradiation annealing treatment, as illustrated in Figures 4.66 and 4.67.

In contrast, prior austenite grain boundaries became significantly more enriched in molybdenum during the annealing treatment, Figure 4.68, whilst lath boundaries showed less of an increase.

The effects of annealing on the phosphorus redistribution closely parallel those of molybdenum, Figure 4.69. Prior austenite grain boundaries were found to become more enriched following annealing, with lath boundaries, if anything, perhaps less so.
Figure 4.64: Effect of post-irradiation annealing on chromium concentration as a function of distance from (a) prior austenite grain boundaries and (b) lath boundaries in irradiated FV448.
Figure 4.65: Effect of post-irradiation annealing at 465°C on nickel concentration as a function of distance from (a) prior austenite grain boundaries and (b) lath boundaries.
Figure 4.66: Effect of post-irradiation annealing at 465°C on silicon concentration as a function of distance from (a) prior austenite grain boundaries and (b) lath boundaries.
Figure 4.67: Effect of post-irradiation annealing at 465°C on manganese concentration as a function of distance from (a) prior austenite grain boundaries and (b) lath boundaries.
Figure 4.68: Effect of post-irradiation annealing at 465°C on molybdenum concentration as a function of distance from (a) prior austenite grain boundaries and (b) lath boundaries.
Figure 4.69: Effect of post-irradiation annealing at 465°C on phosphorus concentration as a function of distance from (a) prior austenite grain boundaries and (b) lath boundaries.
Thus the post-irradiation annealing treatment caused a clear increase in prior austenite grain boundary concentration of the solutes chromium, molybdenum and phosphorus. The depletion of chromium from the matrix towards the boundary plane was lessened. In addition, the enrichment of nickel at boundary planes was reduced, particularly at lath boundaries, following the irradiation temperature anneal.

4.2 Weld zone material

4.2.1 As-tempered

4.2.1.1 Microstructure

The microstructure across the weld zone in the as-tempered condition is shown by the optical micrographs of Figure 4.70. The low magnification view, Figure 4.70(a), shows the extent of the fusion and heat affected zones: the fusion zone being approximately 10 mm in width, with the heat affected zone extending a further 5 mm into the parent plate either side of the fusion zone. Thus the total width of microstructure affected by the welding was about 20 mm. Three distinct morphologies across the weld zone width were observed, shown in the higher magnification micrographs of Figure 4.70(b), (c) and (d). The microstructure of the fusion zone, Figure 4.70(b), consisted of packets of coarse lath martensite oriented generally in the direction of heat flow. The heat affected zone microstructure consisted of polygonal ferrite resulting from effectively overtempering the martensite of the parent plate, Figure 4.70(c). At the interface between the fusion and heat affected zones were occasional blocky shaped regions of δ-ferrite as shown in Figure 4.70(d).

Thin foils from the weld zone examined under the electron microscope had the typical heavily dislocated lath martensite structure as shown in Figure 4.71. Precipitation consisted primarily of small irregularly shaped M$_{23}$C$_6$ particles. There were occasional large precipitates of blocky morphology, as shown in Figure 4.72 for two such precipitates, triangular in cross section, at the foil edge. These were identified by EDX analysis as carbonitrides of principally titanium and niobium, having a metal composition of: 58Ti-23Nb-10Cr-4V-3Fe-1Mo (wt.%). The benefit of the windowless X-ray detector in being capable of detecting and distinguishing the carbon and nitrogen K-peaks at the low energy end of X-ray spectra is clearly shown in a spectrum obtained from one of the nitride particles, Figure 4.72(b).
Figure 4.70: Optical micrographs of off-normal FV448 weld material. (a) Section across weld line revealing extent of weld metal and heat affected zone. Microstructures of: (b) weld metal, (c) heat affected zone and (d) interface between weld metal and heat affected zone.
Figure 4.71: Transmission electron micrograph of off-normal FV448 weld material in the as-tempered condition.
Figure 4.72: (a) Mixed Ti-Nb-Cr carbonitride particles in as-tempered off-normal FV448 weld material. (b) X-ray spectrum from carbonitride particle, showing separate nitrogen and carbon peaks resolved by windowless detector.
4.2.1.2 Composition

The consequence of using the nickel-rich alloy, PE16, as filler material was to raise the nickel content of the fusion zone to a mean concentration of 3.8 wt.% from the 0.6 wt.% of the parent plate. Figure 4.73 shows the variation in nickel and chromium concentration across the weld region from the EDX-ray microanalysis linescan performed using the Stereoscan 360 SEM. This rise in nickel concentration from 0.6 to 3.8 wt.% suggests that the PE16 filler material (43.5 wt.%Ni) constituted approximately 7.5% of the weld pool by weight. The nominal composition of PE16 is: 43.5Ni-34Fe-16.5Cr-3.3Mo-1.2Al-1.2Ti (wt.%). Thus by simple ratio analysis the anticipated composition of the fusion zone should be: 11.1Cr-3.8Ni-0.9Mn-0.8Mo-0.6Si-0.3Nb-0.15V-0.1Ti-0.1Al bal.Fe (wt.%).

Although from Figure 4.73 the composition across the fusion zone seems relatively homogeneous, analysis on a fine scale indicated that this in fact was not so. Characterization by FEGSTEM EDX of lath boundary microchemistry in the fusion zone revealed that one of the pair of laths lying either side of the several analysed lath boundaries was consistently richer in nickel than the other. This phenomenon is graphically illustrated in Figure 4.74, containing data for the mean concentration profiles of chromium, nickel, molybdenum, manganese and silicon across lath boundaries in the fusion zone of as-tempered weld material. The principal effect is the partitioning of nickel between the adjacent laths either side of the interface. The average concentration of nickel in the nickel-rich lath was about 5 wt.%, whilst in the neighbouring lath it was just 2%. From Figure 4.74 there is also evidence of manganese partitioning in the same sense as nickel and the suggestion of chromium, molybdenum and silicon partitioning in the opposite sense. The other notable feature of the lath boundary region microchemistry is the segregation of chromium and, to a lesser extent, molybdenum to the lath boundary planes themselves.

Subsequent to this discovery of solute partitioning apparently between individual laths, X-ray mapping and linescans over greater dimensions were performed to define the scale of the partitioning. An example of digital X-ray mapping a region of the fusion zone is shown in Figure 4.75. The upper left image, Figure 4.75(a), is the digital electron image of the area scanned, formed pixel-wise from the bright field detector showing the lath structure oriented in a horizontal direction. The image at the upper right, Figure 4.75(b), is the corresponding map of chromium distribution; the intensity of each pixel varying in direct proportion to the number of X-ray counts detected in the user-defined chromium Kα X-ray energy window during the analysis time. The small regions of very high chromium concentration, the bright patches in the map, correspond to the chromium-rich
Figure 4.73: Chromium and nickel concentrations as a function of distance transversely across FV448 off-normal weld zone.
Figure 4.74: Mean solute concentration profiles across lath boundaries in as-tempered FV448 off-normal weld zone material.
Figure 4.75: Digital mapping images of off-normal FV448 weld material in the as-tempered condition. (a) Bright field electron image. Corresponding maps of (b) chromium distribution, (c) nickel distribution and (d) a binary map of nickel distribution.
M₂₃C₆ carbide particles. The background distribution of chromium in the matrix is relatively uniform. In contrast, it is evident from the map of nickel concentration, Figure 4.75(c), that there is a heterogeneous distribution of nickel in the lath structure. The distribution is essentially bimodal, with the areas of relatively high and relatively low nickel concentration being approximately uniform in composition. The change in concentration between the low and high nickel areas is abrupt - not continuous. The contrast between the two regions is emphasized in Figure 4.75(d); a binary image of the nickel distribution formed by setting areas above a certain threshold concentration to white, and below it to black. The general orientation of the high/low nickel banding is that of the lath structure orientation. However, the dimensions of the areas of high and low nickel do not correspond to individual laths, but to several.

Analysis of X-ray maps acquired from a different area yield some further results. The electron image of the analysed region is shown in Figure 4.76(a). A feature immediately of note is the abrupt change in image brightness approximately half way down the image. This is a result of the field emission gun's instability for continuous operation over extended periods, as discussed previously. The images are created sequentially, pixel by pixel, acquiring data for the full analysis time at each point before moving on, rather than scanning the whole region more quickly several times over to build a composite picture. Hence any sudden variation in beam current during the analysis time results in a step change in image brightness. The line AA corresponds to the position of the qualitative linescan extracted from the digital elemental maps by the AN10000 software, and to the position of a manually incremented quantitative linescan, described below. The chromium in solution is again seen to be uniformly distributed, with the chromium rich carbides showing clearly in Figure 4.76(b). The bimodal distribution of nickel is again evident in the nickel map, Figure 4.76(c), with the distribution oriented in the lath direction, but on a scale larger than individual lath dimensions. Finally, Figure 4.76(d) is the variation in nickel concentration along the line AA extracted from the acquired mapping data. The vertical scale is in terms of number of X-ray counts detected in the particular energy range for nickel Kα and is thus not quantitative. The sharply defined interfaces between the regions of high and low nickel concentration can be inferred from the steep concentration gradients between them.

A fully quantitative linescan along the same line AA was performed by manually positioning the beam at collinear points and collecting the generated X-ray spectra. Rather than use a stationary probe, as for as the interfacial analysis, the spectra were generated by scanning the probe over an area of 20 x 10 nm in order to reduce scatter. The area scanned was positioned such that its centroid was 30 nm either side of lath
Figure 4.76: Digital mapping images of off-normal FV448 weld material in the as-tempered condition. (a) Bright field electron image. Corresponding maps of (b) chromium distribution, (c) nickel distribution and (d) the linescan AA showing variation of nickel concentration with distance.
Figure 4.77: Manually incremented quantitative linescan along AA in Fig. 4.76, showing the transverse variation in solute concentration across martensite laths in as-tempered off-normal FV448 weld metal.
boundaries lying along the line AA, and at known distances of approximately 200 - 300 nm apart across the laths.

The results for the spatial composition of chromium, nickel, molybdenum and manganese are shown in Figure 4.77. The variation in nickel concentration follows that determined from the digital mapping, rising from about 1.8 - 2.0 wt.% in the low nickel regions to roughly 6 wt.% in the high nickel zones. The chromium concentration is seen to vary slightly, rising from 11.5 to 12.5 wt.% at the two extremes of concentration. The sense of variation is exactly the inverse of the nickel distribution, such that the regions richest in chromium were leanest in nickel and vice versa. The errors associated with the concentration linescans of molybdenum and manganese are relatively larger than for chromium and nickel, and the resultant increase in scatter leads to the variations being less well defined. However, it is apparent that there is a consistent variation in the concentration of the two solutes, with molybdenum showing, the same spatial variation as chromium, and manganese the same as nickel. If the abrupt changes in nickel concentration are compared with the positions of lath boundaries it is evident that the steep concentration gradients always occur at lath boundaries. However, the converse does not necessarily hold true: lath boundaries do not always coincide with large changes in nickel concentration.

4.2.2 Irradiated weld material

4.2.2.1 Microstructure

The microstructure of the neutron irradiated weld zone material was complex and varied according to which part of the weld zone the thin foil was cut from.

4.2.2.1.1 Fusion zone interface region

This area in the as-tempered weld zone material comprised large blocky-shaped regions of δ-ferrite within a matrix of polygonal ferrite in the heat affected zone, adjacent to coarse lath martensite in the fusion zone.

In the weld material irradiated at 400°C the superficial structure remained the same. Large chunks of δ-ferrite adjacent to lath martensite were observed, as shown in Figure 4.78. As with the irradiated parent plate material, direct evidence of displacement damage came from two sources. Firstly there was the presence of rectilinear dislocation loops, as can be seen in Figure 4.79. Secondly, heterogeneously distributed radiation-induced voids were observed, principally in the areas of δ-ferrite, approximately 10-20 nm across and apparently cuboidal in morphology. A number of voids can be seen in Figure 4.80,
Figure 4.78: Microstructure of off-normal FV448 weld material near weld metal/heat affected zone interface. A region of delta ferrite is visible in the upper right of the micrograph adjacent to lath martensite.
Figure 4.79: Fine scale microstructure of off-normal FV448 weld metal irradiated to 30 dpa (NRT) at 400°C. Evidence of displacement damage is shown by the presence of dislocation loops.
Figure 4.80: Void distribution in region of delta ferrite of off-normal FV448 weld material irradiated to 30 dpa(NRT) at 400°C.
Figure 4.81: Void distribution in lath martensitic region of off-normal FV448 weld material irradiated to 30 dpa(NRT) at 400°C.
around a perforation in the foil in a region of $\delta$-ferrite; whilst two cuboidal voids can be resolved in martensite laths in Figure 4.81.

Copious precipitation was observed following irradiation, as indicated by Figure 4.82. Widely distributed $M_23C_6$ was evident, in conjunction with the morphologically similar phase enriched in nickel and silicon that was observed in the parent plate material. Occasional small spheroidal niobium- and vanadium-rich carbide particles about 40 nm in diameter were also detected. On a finer scale still, a very fine dispersion of particles rich in nickel, silicon and manganese were widely distributed. These 10-20 nm particles were found to be present in greater numbers in the regions of $\delta$-ferrite, their average composition being determined as: 60Ni-18Mn-14Si-4Nb-3P-1Mo-0.5V (wt.%).

The microstructure of the interface between the heat affected zone and fusion zone in material irradiated at 465°C was essentially similar to that described above for the material irradiated at 400°C. Dislocation loops and small sparsely distributed radiation-induced voids were again present. The finely distributed population of the nickel-, silicon- and manganese-rich phase is clearly seen in the region of $\delta$-ferrite in Figure 4.83. These particles were arranged in string-like formations, resembling necklace structures, Figure 4.84, suggesting that the precipitates are decorating dislocations. The precipitates themselves have greater definition when dislocations are out of contrast. However, Figure 4.85 does show that these small particles are indeed associated with dislocations. At a still higher magnification, small radiation induced voids are also resolvable in the $\delta$-ferrite, Figure 4.86.

4.2.2.1.2 Fusion zone

The original tempered lath martensite microstructure of the fusion zone was found to be grossly altered following neutron irradiation at 465°C. Figure 4.87 illustrates the resulting irradiated microstructure at a low magnification. There is a distribution of lath shaped second phase, darkened by diffraction contrast, apparently consistently oriented in a certain crystallographic direction within a particular area. This is shown to be the case in Figure 4.88. The upper micrograph is the bright field image showing several of the second phase laths, darkened by diffraction contrast. The lower image is the centred dark field image using one of the second phase reflections, showing all except one of the second phase laths to have the same crystallographic orientation.

Selected area diffraction pattern analysis revealed that the second phase has a face centred cubic structure with a lattice parameter a factor of 1.26 greater than that of the bcc matrix. This leads to a lattice parameter of 3.61Å taking a value of 2.8664Å for bcc iron [199].
Figure 4.82: Precipitate distribution in off-normal FV448 weld material irradiated to 30 dpa(NRT) at 400°C.
Figure 4.83: Fine scale precipitation in region of delta ferrite in off-normal weld material irradiated to 28 dpa(NRT) at 465°C.
Figure 4.84: Necklace-like arrangement of fine precipitation in region of delta ferrite in off-normal FV448 weld material irradiated to 28 dpa(NRT) at 465°C.
Figure 4.85: Fine precipitates in association with dislocation lines in region of delta ferrite in off-normal FV448 weld material irradiated at 465°C to 28 dpa(NRT).
Figure 4.86: Void distribution in region of delta ferrite in off-normal FV448 weld material irradiated to 28 dpa(NRT) at 465°C.
Figure 4.87: Two phase structure of weld metal region in off-normal FV448 weld material irradiated to 28 dpa(NRT) at 465°C.
Figure 4.88: Lath shaped second phase oriented in common direction in weld metal region of off-normal FV448 irradiated to 28 dpa(NRT) at 465°C. Second phase darkened by diffraction contrast in bright field image (a). Centred dark field image using second phase reflection (b).
The published lattice parameter for austenite from the same source is 3.5852Å, thus the lath shaped second phase found after irradiation is austenite.

A similar mixed dense population of precipitates was found in the irradiated fusion zone as in the heat affected zone and parent plate material, as illustrated in Figure 4.89 where large numbers of precipitates are evident in both the ferrite and austenite phases. The lath shaped austenite phase can be seen to contain large irradiation-induced voids. An individual lath is shown in Figure 4.90, where the high density of faceted voids up to 100 nm in diameter is clearly shown.

The consistent alignment of the austenite laths within the matrix suggests that there is a specific orientation relationship between the austenite and ferrite. This was investigated at length by selected area diffraction pattern analysis. However, the precise determination of orientation relationships by this method is difficult. Zone axis determinations in thin foil specimens may be in error by up to 5° since the reciprocal lattice points are extended in the direction parallel to the foil normal [002]. Use of Kikuchi lines can considerably improve upon this, but their useful formation requires a relatively thick foil with a 'clean' microstructure. Certainly with respect to the latter, these specimens fail to fulfil the criteria. The foil was tilted such that both the austenite and ferrite were strongly diffracting and a selected area aperture inserted to form coincident selected area diffraction patterns from the matrix ferrite and two or three laths of austenite as indicated in Figure 4.91.

A number of apparently parallel zone relationships were found between the second phase austenite and matrix ferrite. A total of five thin foils were investigated to determine any orientation relationships. Each foil examined exhibited only two or three of the total number of parallel zone axis combinations seen. Examples of each of the selected area diffraction patterns corresponding to the zone axis relationships are shown in Figures 4.92 through to 4.103. The diffraction spots are indexed beside each pattern and any coincidence of spots or directions from the reciprocal lattice plane given to fully define the orientation relationship.

A total of nine apparent zone axis relationships between the face centred and body centred cubic phases were found, as summarized in Table 13. One of the sets of parallel zone axes, $\bar{1}21_{\text{fcc}} // 3\bar{1}1_{\text{bcc}}$, was found to exist in two forms, the difference being a relative rotation of approximately 14° about the zone axes as can be seen when comparing Figure 4.96 with Figure 4.97. Several instances were found where a single austenite zone axis was parallel to two or more body centred cubic zone axes. Except in one case,
Figure 4.89: Precipitate distribution in ferrite and austenite phases in weld metal region of off-normal FV448 irradiated to 28 dpa(NRT) at 465°C.
Figure 4.90: Void distribution in lath of austenite in weld metal region of off-normal FV448 irradiated to 28 dpa (NRT) at 465°C. Swelling of austenite lath -17%.
Figure 4.91: Illustration of arrangement for determination of orientation relationships between austenite and ferrite. Both phases brought into diffraction contrast and selected area aperture used to define area for production of coincident diffraction patterns for analysis.
Figure 4.92: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.

\[(10\overline{1})_{fcc} \parallel (11\overline{1})_{bcc}\]

\[[111]_{fcc} \parallel [011]_{bcc}\]
Figure 4.93: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.
Figure 4.94: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.
Figure 4.95: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.
Figure 4.96: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.

\[
\begin{align*}
\langle 1 \bar{2} 1 \rangle_{\text{fcc}} & \parallel \langle 31 \bar{1} \rangle_{\text{bcc}} \\
\{10\bar{1}\}_{\text{fcc}} & \parallel \{233\}_{\text{bcc}} \\
\{1\bar{1}1\}_{\text{fcc}} & \parallel \{011\}_{\text{bcc}}
\end{align*}
\]
Figure 4.97: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.
Figure 4.98: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.
Figure 4.99: Selected area diffraction pattern exhibiting an indexed and defined coincident zone axis relationship between austenite and ferrite phases.
Figure 4.100: Selected area diffraction pattern exhibiting two indexed and defined coincident zone axis relationships between austenite and ferrite phases.
Figure 4.101: Selected area diffraction pattern exhibiting two indexed and defined coincident zone axis relationships between austenite and ferrite phases.
Figure 4.102: Selected area diffraction pattern exhibiting three indexed and defined coincident zone axis relationships between austenite and ferrite phases.
Figure 4.103: Selected area diffraction pattern exhibiting two indexed and defined coincident zone axis relationships between austenite and ferrite phases.
Table 13

Summary of observed orientation relationships between austenite and ferrite in off-normal FV448 weld metal irradiated at 465°C.

<table>
<thead>
<tr>
<th>Coincident zone axes</th>
<th>Parallel directions</th>
<th>Orientation relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>10(\bar{1})<em>{fcc} // (\bar{1})1(\bar{1})</em>{bcc}</td>
<td>11(\bar{1})<em>{fcc} // 011</em>{bcc}</td>
<td>K-S</td>
</tr>
<tr>
<td>12(\bar{1})<em>{fcc} // 2(\bar{1})1</em>{bcc}</td>
<td>10(\bar{1})<em>{fcc} // 11(\bar{1})</em>{bcc}</td>
<td>K-S</td>
</tr>
<tr>
<td>12(\bar{1})<em>{fcc} // 31(\bar{1})</em>{bcc}</td>
<td>10(\bar{1})<em>{fcc} // 23(\bar{3})</em>{bcc}</td>
<td>(K-S)*</td>
</tr>
<tr>
<td>12(\bar{1})<em>{fcc} // 3(\bar{2})1</em>{bcc}</td>
<td>10(\bar{1})<em>{fcc} // 11(\bar{1})</em>{bcc}</td>
<td>(K-S)*</td>
</tr>
<tr>
<td>10(\bar{1})<em>{fcc} // 100</em>{bcc}</td>
<td>11(\bar{1})<em>{fcc} // 011</em>{bcc}</td>
<td>N-W</td>
</tr>
<tr>
<td>12(\bar{1})<em>{fcc} // 0(\bar{1})1</em>{bcc}</td>
<td>10(\bar{1})<em>{fcc} // 100</em>{bcc}</td>
<td>N-W</td>
</tr>
<tr>
<td>11(\bar{1})<em>{fcc} // 0(\bar{1})2</em>{bcc}</td>
<td>10(\bar{1})<em>{fcc} // 100</em>{bcc}</td>
<td>(N-W)*</td>
</tr>
<tr>
<td>100_{fcc} // 110_{bcc}</td>
<td>0(\bar{1})1_{fcc} // 1(\bar{1})1_{bcc}</td>
<td>Pitsch</td>
</tr>
<tr>
<td>12(\bar{1})<em>{fcc} // 31(\bar{1})</em>{bcc}</td>
<td>1(\bar{1})3_{fcc} // 1(\bar{1})2_{bcc}</td>
<td>NR</td>
</tr>
</tbody>
</table>

K-S : Kurdjumov - Sachs
N-W : Nishiyama - Wasserman
NR : Not resolvable

*(Parentheses denote close, but not exact, agreement.)
\[ \{\{2\{1\}_\text{fcc} \parallel 3\{2\}_\text{bcc} \} \text{ (Figure 4.103)} \], these were all duplications of the single orientation zone axis relationships.

Despite the large number of apparently dissimilar zone axis relationships found, the orientation relationships between the austenite and ferrite phases defined by the zone axes and coincidence of diffraction spots or directions were predominantly consistent with one or other of two unique relationships. The two distinct relationships are firstly the Kurdjumov-Sachs relationship \cite{201} defined by:

\begin{align*}
1\{1\}_\text{fcc} & \parallel 0\{1\}_\text{bcc} \\
1\{0\}_\text{fcc} & \parallel 1\{1\}_\text{bcc} \\
1\{2\}_\text{fcc} & \parallel 2\{1\}_\text{bcc}
\end{align*}

and secondly the Nishiyama-Wasserman relationship \cite{202,203} defined by:

\begin{align*}
1\{1\}_\text{fcc} & \parallel 0\{1\}_\text{bcc} \\
1\{0\}_\text{fcc} & \parallel 1\{0\}_\text{bcc} \\
1\{2\}_\text{fcc} & \parallel 0\{1\}_\text{bcc}
\end{align*}

The coincident zone axes of \((10\{1\}_\text{fcc} \parallel (1\{1\}_\text{bcc})\) and \((1\{2\}_\text{fcc} \parallel (2\{1\}_\text{bcc})\) shown in Figures 4.92 and 4.93 respectively are in exact agreement with the Kurdjumov-Sachs relationship. Similarly the zone axis coincidences of \((10\{1\}_\text{fcc} \parallel (1\{0\}_\text{bcc})\) and \((1\{2\}_\text{fcc} \parallel (0\{1\}_\text{bcc})\), Figures 4.94 and 4.95, agree fully with the Nishiyama-Wasserman relationship.

The relationship defined by the coincident selected area diffraction patterns in Figure 4.96 of:

\begin{align*}
(1\{2\}_\text{fcc} & \parallel (3\{1\}_\text{bcc}) \\
[10\{1\}_\text{fcc} & \parallel [2\{3\}_\text{bcc}] \\
[1\{1\}_\text{fcc} & \parallel [0\{1\}_\text{bcc}]
\end{align*}

is not in exact agreement with either the Kurdjumov-Sachs or the Nishiyama-Wasserman relationships. However, reference to a stereogram of the Kurdjumov-Sachs relationship, Figure 4.104, reveals that the \([2\{2\}_\text{fcc} \parallel [3\{1\}_\text{bcc}]\) zone axes are only 0.5° apart for that
Figure 4.104: Stereogram with major pole coincidences of the bcc and fcc lattices in the Kurdjumov-Sachs orientation relationship, showing $3\overline{1}1_{\text{bcc}}$ to be just 0.50° from $2\overline{1}1_{\text{fcc}}$ and, similarly, $\overline{1}32_{\text{bcc}}$ to be just 0.36° from $121_{\text{fcc}}$. 

\begin{align*}
[111]_{\text{fcc}} &= [011]_{\text{bcc}} \\
[10\overline{1}]_{\text{fcc}} &= [11\overline{1}]_{\text{bcc}} \\
[1\overline{2}1]_{\text{fcc}} &= [2\overline{1}1]_{\text{bcc}}
\end{align*}
particular variant of the Kurdjumov-Sachs relationship. This is less than the probable error in determination of precise zone axes by this method. Similarly for the coincident selected area diffraction patterns defining the relationship:

\[(\bar{1}21)_{fcc} \parallel (3\bar{2}1)_{bcc}\]

\[[10\bar{1}]_{fcc} \parallel [11\bar{1}]_{bcc}\]

\[[111]_{fcc} \parallel [145]_{bcc}\]

in Figure 4.103 it can be shown that the \([121]_{fcc}\) and \([\bar{1}32]_{bcc}\) zone axes are only 0.36° apart for another variant of the Kurdjumov-Sachs relationship, Figure 4.104.

The relationship defined by the coincident selected area diffraction patterns in Figure 4.98 of:

\[(\bar{1}1\bar{1})_{fcc} \parallel (0\bar{1}2)_{bcc}\]

\[[10\bar{1}]_{fcc} \parallel [100]_{bcc}\]

\[[121]_{fcc} \parallel [021]_{bcc}\]

is shown in the stereogram of Figure 4.105. From this it is found that for a variant of the Nishiyama-Wasserman relationship the \([1\bar{1}1]_{fcc}\) and \([0\bar{1}2]_{bcc}\) zone axes are 1.04° apart.

Considering now the coincident diffraction patterns formed in Figure 4.99 which define the relationship:

\[(\bar{1}00)_{fcc} \parallel (\bar{1}10)_{bcc}\]

\[[0\bar{1}\bar{1}]_{fcc} \parallel [\bar{1}1\bar{1}]_{bcc}\]

\[[01\bar{1}]_{fcc} \parallel [\bar{1}\bar{1}1]_{bcc}\]

This relationship cannot be resolved into either the Kurdjumov-Sachs or Nishiyama-Wasserman relationship. Instead it is a variant of the less commonly observed Pitsch relationship \([204]\). This relationship is in fact the inverse of the Nishiyama-Wasserman correspondence: that is, the crystal structures of the indices defining the Nishiyama-Wasserman relationship are exchanged. It should be noted that this relationship was observed only once in one particular foil.

The final zone axis relationship observed, in Figure 4.97, defined by:

\[(\bar{1}\bar{2}1)_{fcc} \parallel (3\bar{1}1)_{bcc}\]

\[[\bar{1}1\bar{3}]_{fcc} \parallel [\bar{1}\bar{1}2]_{bcc}\]
Figure 4.105: Stereogram with major pole coincidences of the bcc and fcc lattices in the Nishiyama-Wasserman orientation relationship, showing $0\bar{1}2_{bcc}$ to be just $1.04^\circ$ from $\bar{1}1\bar{1}_{fcc}$. 

\begin{align*}
[\bar{1}\bar{1}\bar{1}]_{fcc} & \parallel [0\bar{1}1]_{bcc} \\
[10\bar{1}]_{fcc} & \parallel [100]_{bcc} \\
[1\bar{2}1]_{fcc} & \parallel [0\bar{1}1]_{bcc}
\end{align*}
Figure 4.106: Stereogram constructed for the apparent zone axis relationship between bcc and fcc phases observed in Fig.4.97: \( \{211\text{fcc} \parallel 311\text{bcc} \) and \( [113\text{fcc} \parallel 112\text{bcc}]. \)
**Figure 4.107**: Two phase structure of weld metal region in off-normal FV448 irradiated to 28dpa(NRT) at 465°C exhibiting Nishiyama-Wasserman relationship. (a) Bright field image, (b) coincident selected area diffraction patterns and centred dark field images using (c) austenite reflection and (d) ferrite reflection.
Figure 4.108: Two phase structure of weld metal region in off-normal FV448 irradiated to 28 dpa(NRT) at 465°C exhibiting Kurdjumov-Sachs relationship. (a) Bright field image, (b) coincident selected area diffraction patterns and centered dark field images using (c) austenite reflection and (d) ferrite reflection.
does not obviously correspond to any of the aforementioned relationships - nor indeed to the Bain relationship \[205\]. The stereographic projections for cubic crystals in the \([1\bar{2}1]\) and \([3\bar{1}1]\) zone axes have been constructed with low index poles plotted. These have been superimposed at a relative angle such that the respective poles \([\bar{1}13]\) and \([\bar{1}12]\) are also coincident, as shown in Figure 4.106. From this it may be seen that the orientation relationship described by the coincident selected area diffraction patterns is not apparently resolvable into a simpler relationship. Of the three previously observed relationships and the Bain relationship it is closest to the Pitsch, being approximately 4° removed from it.

The manifestation of variants of both the Nishiyama-Wasserman and Kurdjumov-Sachs relationships are shown in Figures 4.107 and 4.108 respectively. The upper left micrograph of Figure 4.107 is a bright field image of an area containing several austenite laths running vertically, with both the austenite and ferrite matrix darkened by diffraction contrast. The coincident selected area diffraction patterns of the two phases are shown in the upper right image, with the two operating reflections used for the centred dark field austenite and ferrite images, shown in the lower left and right micrographs of Figure 4.107, ringed.

Similarly for the Kurdjumov-Sachs relationship shown in Figure 4.108. The upper left bright field image, darkened by diffraction contrast, is of a larger area, 4 x 3.5 μm, containing a number of austenite laths. The coincident selected area diffraction patterns are shown in the upper right image. The austenite laths are clearly shown in the lower left centred dark field image, whilst the ferrite matrix shows in the lower right centred dark field image, using the operating reflections indicated in the coincident electron diffraction pattern. The relationship between the austenite and ferrite evidently holds over a large area.

4.2.2.2 Microchemistry

4.2.2.2.1 Martensite-ferrite interface

Solute concentration profiles were generated across tempered martensite / \(\delta\)-ferrite interfaces in the heat affected zones of weld material irradiated at 400 and 465°C. The results are summarized in Figures 4.109 and 4.110, showing the mean solute concentration profiles obtained from three boundaries in each case.

For both irradiation temperatures we see enrichment of all solutes at the boundary plane. The enrichment for each solute was found to be greater after irradiation at 400°C than at 465°C, except for molybdenum in which case the two concentration profiles were similar. There are indications of slight partitioning of the ferrite forming elements chromium and,
Figure 4.109: Mean solute concentration profiles across ferrite/martensite interfaces in off-normal FV448 weld irradiated at 400°C.
Figure 4.110: Mean solute concentration profiles across ferrite/martensite interfaces in off-normal FV448 weld irradiated at 465°C.
particularly, molybdenum. Both solutes were found to be present at consistently higher concentrations in the $\delta$-ferrite.

4.2.2.2 Austenite-ferrite interface

The mean solute concentration profiles measured across austenite / ferrite interfaces in the fusion zone of weld material irradiated at 465°C are shown in Figure 4.111, taken from five such interfaces. Immediately striking is the considerable partitioning of chromium, nickel and manganese between the two phases. The austenite stabilizing elements nickel and manganese can clearly be seen to reside preferentially in the austenite phase. So too, however, does the ferrite forming element chromium; its concentration rising with increasing distance from the interphase boundary to almost 20 wt.% in the austenite from around 8 wt.% in the ferrite.

As well as partitioning between the two phases, nickel was seen to be substantially enriched at the boundary plane. Silicon, too, was also found to be slightly enriched at the austenite / ferrite interface. Profiles for other solutes, including phosphorus and molybdenum, were relatively uniform across the interface, showing no discernible partitioning between the two phases and neither enrichment nor depletion at the interfacial plane within the scatter of experimental results.

4.2.2.2.3 Void interfaces - austenite

The spatial variation in microchemistry adjacent to several voids induced in the austenitic second phase was measured. Figure 4.90 revealed that these voids tended to exhibit a faceted morphology. For EDX-ray analysis using the FEGSTEM, the foil was tilted such that one of the planar void surfaces was made parallel to the incident electron beam. Additionally the void surface was chosen such that, as far as possible, it lay perpendicular to the major axis of the lath-shaped austenite phase. This then meant that the linear compositional profile across the void interface was generated approximately parallel to the lath edges and hence any influence of the solute concentration field associated with the interphase boundary remained fairly constant.

The set of mean solute concentration profiles adjacent to voids in the austenite phase is shown in Figure 4.112. The data represent mean values from six such voids. The profiles shown can be divided into two categories: those solutes relatively enriched at the void surface and those becoming depleted. In the category of solutes being enriched at the void surface fall nickel, silicon and aluminium. The solutes found to be depleted were chromium, manganese and molybdenum. There were suggestions at a few of the void interfaces of slight phosphorus and titanium enrichment. However, the considerable
Figure 4.111: Mean solute concentration profiles across austenite/ferrite interfaces in off-normal FV448 weld irradiated at 465°C.
Figure 4.112: Mean solute concentration as a function of distance from void interfaces in austenite in FV448 weld irradiated at 465°C.
variation in the determined concentrations led to the standard error of each mean data point being as great as the absolute mean value itself and thus not statistically reliable.

4.2.2.2.4 Void interfaces-ferrite

Solute concentration profiles were generated from adjacent to several of the occasional very fine voids found in the ferrite phase. These voids appeared more spherical in morphology when imaged in the FEGSTEM, not having such well defined planar internal faces as those seen in the austenite laths. The dark contrast rim in the void image was taken to be the void edge. The voids were observed only in the very thinnest parts of the foil, calculated at between 20 - 30 nm in thickness by the relative number of X-ray counts generated from through the centre of the void of known diameter and slightly removed from the void. The average void diameter was approximately 10 nm, so the total thickness of material above and below the void was between 10 and 20 nm. When analysing the chemical composition using a stationary probe at a series of points across the void into the matrix, material was sputtered away by the electron beam to form a keyhole-shaped image. This is shown by the Polaroid micrographs taken from the STEM image in Figure 4.113. Presumably the material between the bottom surface of the void and the foil exit surface becomes sputtered away under the intense electron beam. The width of the slot sputtered away, measured from the images, is approximately 4 nm, compared to the nominal 3.5 nm incident probe diameter, implying that there is very little beam spreading for these specimen thicknesses.

The mean solute concentration profiles adjacent to voids in the ferrite phase of the weld material irradiated at 465°C are shown in Figure 4.114 whilst the corresponding profiles for the lower irradiation temperature of 400°C are shown in Figure 4.115. In the material irradiated at 465°C there seems little systematic variation in spatial solute concentration adjacent to the analysed voids. The profiles obtained from the material irradiated at the lower irradiation temperature of 400°C revealed the faint suggestions of nickel and silicon enrichment at the void interface. The profile obtained for chromium showed the more complex situation of depletion towards the void, but with the interfacial concentration remaining as high as the matrix and thus enriched relative to the immediately adjacent material - akin to the profiles obtained at grain boundaries described previously for parent plate material.

4.2.2.2.5 X-ray mapping

As with the unirradiated weld material, digital X-ray mapping was performed on the irradiated weld material. Results from one two phase region from the fusion zone of material irradiated at 465°C are illustrated in Figure 4.116.
Figure 4.113: FEGSTEM images of voids in delta ferrite (a) before and (b) after EDX point analyses of interfacial microchemistry using fine electron probe.
Figure 4.114: Mean solute concentration as a function of distance from void interfaces in ferrite in FV448 weld irradiated at 465°C.
Figure 4.115: Mean solute concentration as a function of distance from void interfaces in ferrite in FV448 weld irradiated at 400°C.
The upper left image is the bright field electron image of the field of view containing several voided austenite laths and intragranular precipitation in a ferrite matrix. The middle left image shows the distribution of X-ray counts from the chromium K$_\alpha$ energy window, whilst the lower left image shows the corresponding distribution of nickel K$_\alpha$ X-ray counts detected. Both elemental X-ray maps clearly show a greater number of counts arising from the austenite laths. However this does not inevitably lead to the conclusion that there was an increased concentration of the two elements within these laths, since it was found that the laths of austenite were considerably thicker than the surrounding ferrite matrix owing to preferential polishing, thus giving rise to a proportionately greater number of X-ray counts. Thus, even if the composition of both phases were identical, the variation in thickness would render a spatially non-uniform generation of X-rays. Hence an energy window was defined in the low energy region of the spectrum, away from characteristic X-ray peaks, to detect the continuous Bremsstrahlung radiation. The magnitude of this is proportional to the local mass thickness. Its distribution is shown in the upper right map: Figure 4.116(b). The austenite laths are clearly defined and so too are several of the voids within the austenite laths.

The image processing capability of the Link AN10000 microanalysis system allows the manipulation of acquired images. Thus the raw chromium and nickel X-ray maps, Figure 4.116(c) and (d) were scaled pixel-wise to the 'background' X-ray map to correct for thickness variations. These scaled maps are shown in the middle and lower right images of Figure 4.116 respectively. Even after this scaling, the austenite laths can be seen to be richer in both chromium and nickel. Several large chromium-rich precipitates are revealed, principally within the austenite laths, whilst more numerous, smaller, nickel-rich precipitates are particularly evident in the ferrite matrix when compared with the bright field electron image.

This solute distribution within the ferrite and austenite phases was confirmed by performing a manually incremented linescan across a lath of austenite into the ferrite either side of it. The linescan was aligned so that it also traversed a void contained within the austenite phase. The results of this linescan are given in Figure 4.117, showing the variation in solute concentration with distance. Several effects are noticeable. Firstly, there is clear solute partitioning between the two phases: chromium, nickel, molybdenum and manganese all reside preferentially in the austenite phase. Secondly, segregation of nickel and silicon to the interphase boundary is evident. Thirdly, at the void interface strong enrichment of nickel and, to a lesser extent, of silicon is observed. Finally, depletion of chromium from near to the void in the centre of the austenite lath is also evident.
Figure 4.116: Digital mapping of two phase structure in off-normal FV448 weld metal irradiated at 465°C to 28 dpa(NRT). (a) Bright field electron image, (b) normalising count distribution, (c) chromium distribution, (d) normalised chromium distribution, (e) nickel distribution and (f) normalised nickel distribution.
Figure 4.117: Manually incremented quantitative linescan showing variation in solute concentration across an austenitic lath and void induced in off-normal FV448 weld metal irradiated at 465°C.
CHAPTER FIVE
Discussion

5.1 Parent plate

5.1.1 Microstructure

5.1.1.1 As-tempered condition

The microstructure observed in the FV448 parent plate material following the initial austenitization and tempering treatment was essentially as reported by other workers for this and similar 12%Cr stainless steels, as described in Section 2.1. The high carbon martensite formed by shear transformation during cooling from the austenitization temperature decomposes during the tempering treatment via the precipitation of fairly coarse, irregularly shaped chromium-rich $\text{M}_\text{23}\text{C}_6$ at nucleation sites, principally prior austenite and lath boundaries, with spherical intragranular NbC particles also present.

5.1.1.2 Aged condition

Ageing the FV448 parent plate material at 400°C for 6840 hours or 465°C for 6336 hours was found not to alter significantly the microstructure or precipitate population. That the as-tempered microstructure, established during tempering at 750°C, should be resistant to changes in dislocation density and subgrain evolution during even long term ageing at the much lower temperatures of 400 and 465°C seems reasonable. The Holloman-Jaffe parameter $[206]$, $T(20 + \log t)$, is often used to correlate time and temperature for equivalent tempering treatments, where $T$ is the absolute temperature and $t$ the time at temperature. For ageing at 400°C the time at temperature equivalent to the 6 hours at 750°C tempering treatment is $3.8 \times 10^{11}$ hours. Even at the higher ageing temperature of 465°C the equivalent time becomes $6.3 \times 10^8$ hours.

The absence of any apparent Laves phase formation at either ageing temperature is in accordance with the observations of other ageing studies specifically of FV448. In a study of FV448 aged at 460 and 600°C for 8250 hours Stoter and Little $[60]$ only detected Laves phase at the higher ageing temperature of 600°C and not after ageing at 460°C. The formation of Laves phase seems critically dependent upon the initial composition of the material under investigation, as demonstrated by Hosoi et al $[63]$ and also Maziasz and Klueh $[61]$. Hosoi et al detected the formation of Laves phase down to a lower limiting temperature of approximately 460°C in 9Cr-2Mo steels containing between 0.29 and 0.67%Si aged for up to 1000 hours, Figure 2.13. Removing the silicon from the initial steel composition was effective in raising the lower temperature limit for Laves phase formation to about 600°C. Maziasz and Klueh $[61]$, investigating two heats of a
9Cr-1MoVNb steel, found Laves phase to be formed after ageing for 25000 hours at even their lowest ageing temperature of 482°C. At this temperature the volume fraction of Laves phase detected was far greater in the heat containing 0.4%Si than in the heat containing 0.11%Si, whereas at higher temperatures the dependence on silicon concentration was not so marked.

From these reported observations it is clear that the ageing temperature of 465°C is very close to the lower limit for Laves phase formation in molybdenum-containing 9-12%Cr steels. The heat of FV448 under investigation in this work had a slightly lower silicon concentration than the material used in Stoter and Little's study [60] - 0.38% compared with their 0.46%. Given that a greater silicon concentration has been shown to promote Laves formation, the absence of Laves phase in this work is consistent with the observations of Stoter and Little who did not detect its formation in their higher silicon heat. It should be noted that whilst extraction replicas were not taken to perform a detailed precipitate analysis, there were no apparent grain boundary films running along prior austenite boundaries, characteristic of the morphology of Laves phase. This point will be returned to when discussing the interfacial microchemistry of the aged material, Section 5.1.2.2.

5.1.1.3 Irradiated condition

As expected, high dose fast neutron irradiation was found to radically alter the microstructure of as-tempered FV448 parent plate. Previous work has discussed the effects of neutron irradiation on dislocation and boundary structures, void and dislocation loop formation and precipitate development in FV448 and similar 12%Cr steels [60,61,179-187,207]. This study was aimed more specifically at determining the effects of neutron irradiation on interfacial microchemistry, thus a detailed investigation of dislocation and void structures was not performed. However, the observed microstructural features are in agreement with previous investigations; a distinct lowering of dislocation density and the formation of subgrains at the higher irradiation temperature, the presence of rectilinear $a(100)$ and smaller circular $\frac{1}{2}a(111)$ dislocation loops and the almost complete absence of voids confirming the well known very high resistance this class of materials has to void swelling under irradiation.

Stoter and Little [60] carried out a comprehensive study of precipitate development in FV448 fast neutron irradiated to comparably high doses at similar temperatures to the material in this work. Thus although an exhaustive survey of precipitate phases in this material was felt to be unnecessary, EDX analysis was used to identify phases present by their chemical fingerprints, since the composition of any radiation-induced phases can
provide indirect evidence to the dynamic behaviour of solutes under irradiation. Two precipitate phases not detected in the aged material were found - both highly enriched in nickel and silicon. The first of these phases was present as 100-200 nm irregularly shaped particles often nucleated adjacent to existing M\textsubscript{23}C\textsubscript{6} precipitates, its typical composition being (wt.%): 20Fe-33Cr-19Ni-13Si-9Mo-2Mn-2V-1N6-1P. The morphology and composition of this phase both suggest that it is M\textsubscript{6}X as seen by Stoter and Little \cite{60} in their FV448 irradiated at 380, 420 and 460°C, and by other workers in 12%Cr steels irradiated in the temperature range 400 to 500°C \cite{188}.

The second of these phases was present as a very fine intragranular dispersion of approximately 20 nm diameter particles of typical composition (at.%): 65Ni-17Si-14Mn-2.5P-1Mo-0.6V-0.5Nb. The morphology of this phase and its composition with reference to Table 5 suggest that it is a form of G phase. This phase was not observed by Stoter and Little in their study of neutron irradiated FV448, but has been detected by Gelles and Thomas \cite{182} and Maziasz \textit{et al} \cite{183} in HT-9 to have a composition varying from the ideal of M\textsubscript{6}Ni\textsubscript{16}Si\textsubscript{7}, where M is usually manganese.

It is immediately apparent from the typical compositions of both these radiation-induced phases that they are significantly enriched in nickel and silicon and, to a lesser extent, phosphorus when compared both to the matrix and M\textsubscript{23}C\textsubscript{6}. Nickel and silicon are present in the bulk at concentrations below their solubility limits in iron. If these phases are the result of local solute supersaturations arising from radiation-induced segregation to defect sinks then the implication is that nickel, silicon and phosphorus each segregate strongly to point defect sinks under the influence of neutron irradiation.

### 5.1.2 Microchemistry

#### 5.1.2.1 As-tempered condition

The grain boundary microchemistry of FV448 in the as-tempered condition, whilst not completely uniform, did not show large variations in solute concentration across the boundary planes. There was a very slight increase in detected chromium, molybdenum and phosphorus concentrations at prior austenite grain boundary planes only. The same observation of slight chromium, molybdenum and phosphorus enrichment only at prior austenite grain boundaries in a quenched and tempered 9Cr-1Mo steel has also been reported by Vatter and Titchmarsh \cite{64}. As set out in Section 2.1.4 an austenitization and tempering treatment gives the opportunity for both non-equilibrium segregation and equilibrium segregation to occur. In principle, this slight enrichment could arise from vacancy-coupled non-equilibrium segregation to boundary planes occurring either during
the cool from the austenitization temperature or the annealing out of any retained vacancy supersaturation during the tempering treatment; or from equilibrium segregation to boundary planes during tempering.

Vacancy-coupled non-equilibrium segregation is, by its non-equilibrium nature, only transient in manifestation. Prolonged high temperature exposure will cause any non-equilibrium concentration of solute dragged to point defect sinks by the vacancy flux to diffuse back down its own concentration gradient and thus re-homogenize the material. Whilst the tempering treatment here of six hours at 750°C could not be considered long term ageing it is certainly prolonged high temperature exposure in terms of the elimination of the excess vacancy concentration and subsequent back-diffusion of any segregated solute.

Faulkner [54] has analysed the behaviour of alloying elements in DIN 1.4914 (the German analogue of FV448) during cooling and tempering treatments. He found that with the exception of boron (which is not present in FV448) all of the solutes could become segregated at interfaces during typical cooling from austenitization. However, subsequent tempering at 700°C for just 1 hour was shown to remove most of the effects of non-equilibrium segregation. The material in this study was even more heavily tempered and is thus unlikely to exhibit remnants of non-equilibrium segregation after tempering.

The alternative to non-equilibrium segregation as a mechanism for the slight detect enrichment of chromium, molybdenum and phosphorus at prior austenite grain boundaries is equilibrium segregation. The interfacial equilibrium concentration of a solute, \( C_b \), was given in Section 2.1.4.1 as:

\[
C_b = \frac{C_s \exp \left( \frac{\Delta G}{RT} \right)}{1 + C_s \exp \left( \frac{\Delta G}{RT} \right)}
\]

where \( C_s \) is the soluble matrix concentration of the solute, \( \Delta G \) is the free energy change associated with the segregation and \( R \) and \( T \) are the gas constant and absolute temperature respectively. Guillou et al [45] analysed results from a temper embrittled 12%Cr steel containing 1%Mo to determine the segregating free energy for the three solutes in question: chromium, molybdenum and phosphorus. Their analysis yielded the conclusions that the intrinsic free energies for segregation of chromium and molybdenum were negligible, thus \( \Delta G_{Cr} = \Delta G_{Mo} = 0 \). Hence as individual solutes in a bcc iron matrix there is no tendency for either chromium or molybdenum segregation to take place. They
did, however, report a large free energy change for phosphorus segregation: $\Delta G_p = 46 \text{ kJ mol}^{-1}$. Using this value for the free energy of phosphorus segregation yields an interfacial phosphorus concentration at equilibrium of 1.32 at.% at a temperature of 750°C for a matrix concentration of 0.006%. This represents an enrichment factor, $\alpha = C_b / C_g$, of 220 over the matrix concentration. The approach to equilibrium is dynamic and thus the kinetics of the segregation need to be considered. The equation governing the accumulation of the monolayer of equilibrium segregant is given by [29]:

$$\frac{C_x - C_g}{C_b - C_g} = 1 - \exp\left(\frac{4Dt}{\alpha^2 d^2}\right) \text{erfc}\left(\frac{4Dt}{\alpha^2 d^2}\right)^{1/2}$$

where $C_x$ is the concentration of solute on the boundary after time $t$, $\alpha$ is the enrichment factor $C_b / C_g$, $d$ is the width of the boundary and $D$ the diffusivity of the solute in the matrix. For a tempering treatment of six hours at 750°C, taking the value for the bulk diffusivity of phosphorus in ferritic iron, $D_p = 0.048 \exp(-183 \, 100 / RT) \text{ cm}^2 \text{ s}^{-1}$ [208], the above equation predicts that $C_x = C_b$. Thus the tempering treatment is predicted to be sufficiently long for equilibrium to be reached.

The theoretical equilibrium concentration of 1.32 at.% phosphorus covering the interfacial monolayer translates to approximately 0.36 wt.%, compared with a mean detected boundary concentration of 0.11 ± 0.08 wt.%. The apparent boundary concentration detected by FEGSTEM is less than the true boundary concentration by a factor dependent upon the relative geometry of the incident probe and the interfacial boundary layer. This is modelled analytically in the next section to analyse the results from the aged material where greater boundary solute concentrations lead to better statistics.

As noted above, from Guillou et al.'s [45] work it was concluded that neither molybdenum nor chromium have any intrinsic free energy of segregation in bcc iron, but such substitutional solutes were reported to interact strongly with phosphorus. They ascribed the following values to the interaction coefficients between solutes and phosphorus; $\Delta G_{\text{Mo-P}} = 37.5 \text{ kJ mol}^{-1}$ (−0.4 eV), $\Delta G_{\text{Cr-P}} = 17 \text{ kJ mol}^{-1}$ (−0.18 eV), $\Delta G_{\text{Ni-P}} = \Delta G_{\text{Mn-P}} = 10.5 \text{ kJ mol}^{-1}$ (−0.1 eV) and $\Delta G_{\text{C-P}} = -9 \text{ kJ mol}^{-1}$ (−0.09 eV). The large positive interaction coefficients between molybdenum and chromium in particular with phosphorus provide the driving force for their interfacial enrichment if phosphorus itself is preferentially resident at boundary planes. Thus the term interactive cosegregation was used to describe the observed behaviour of the solutes chromium, molybdenum and phosphorus. The precise nature of the mechanism for the observed enrichment of all three solutes in tempered steels is disputed in the literature, Section 2.1.4.1, since the role
of carbon invariably interferes. This point too is developed further in the following section discussing the interfacial microchemistry of the aged parent plate material.

5.1.2.2 Aged condition

The grain boundary microchemistry of FV448 parent plate material after ageing at both 400 and 465°C showed significant enrichment of all solutes at the boundary planes. In general, ageing at 465°C promoted greater enrichment than ageing at 400°C, and prior austenite grain boundaries attracted greater solute concentrations than lath boundaries. The greatest boundary plane enrichment relative to the matrix was for phosphorus, whilst the greatest absolute enrichment was of molybdenum.

The fractional monolayer coverages predicted for phosphorus by McLean’s [29] model, above, are 18.2% at 400°C and 9.8% at 465°C. As expected, equilibrium segregation is predicted to be greater at lower temperatures. However, this was not what was experimentally observed in FV448 after ageing at the two different temperatures. The mean boundary plane phosphorus concentrations detected at prior austenite grain boundaries were 0.43 ± 0.09 wt.% and 1.16 ± 0.22 wt.% in material aged at 400 and 465°C respectively. This relative temperature inversion of the magnitude of the segregation may be accounted for by the kinetics of the equilibrium segregation process. The time to accumulate the segregated layer is governed principally by the bulk diffusivity of the solute in question, which is of course in turn exponentially related to the absolute temperature. Using the above equation defining the kinetic approach to equilibrium it is found that at 465°C 6336 hours is in fact long enough for the material to effectively approach equilibrium. At 400°C, however, the situation is changed. The bulk diffusivity of phosphorus at 400°C is a factor of 224 less than at 465°C and the ageing time of 6840 hours at this temperature is now insufficient to reach the predicted equilibrium concentration of 18.2% of a monolayer. Calculation reveals that the theoretical impurity concentration of phosphorus on the boundary at 400°C will reach 4.6% monolayer coverage after 6840 hours.

This theoretical treatment thus suggests interfacial phosphorus concentrations of 9.8 at.% after the 465°C ageing and 4.6% after ageing at 400°C. These figures translate to approximately 3.0 wt.% and 1.4 wt.% respectively; a ratio between the two temperatures of 2.2. The ratio between the experimentally determined phosphorus concentrations in the two aged conditions of FV448 was 2.7. Thus the experimentally observed effect of temperature on the relative interfacial phosphorus concentrations is in close accordance with the relative effect of temperature predicted by theoretical treatment of equilibrium segregation. It is clear, however, that the absolute values of phosphorus segregation
detected experimentally are significantly lower than those predicted by theory. This arises from the finite size of the electron probe. The experimentally derived concentration profile is in fact a convolution of the true solute distribution and the electron distribution of the incident beam. This segregant/electron beam convolution is modelled analytically below, following a discussion of the segregation of other solutes, chromium and molybdenum in particular, and their influence or otherwise on the magnitude of phosphorus segregation.

The increase in phosphorus concentration at grain boundaries in ferritic materials held in the temperature range of 350 to 600°C via equilibrium segregation is well known and is responsible for the phenomenon of temper embrittlement \[39\cdot42\]. Evidence for the interactive cosegregation of molybdenum and chromium in particular with phosphorus is not unequivocal. Certainly chromium and molybdenum enrichments have often been found in combination with, and in proportion to, phosphorus segregation at grain boundaries, Section 2.1.4.1. However, more recent work has suggested that the greater enrichment of phosphorus found at boundaries in chromium containing steels is caused not by the interactive cosegregation of the two elements, but by the reduction in grain boundary carbon activity prompted by chromium. Carbon is even more surface active than phosphorus, with a reported segregation free energy of 92.4 kJ mol\(^{-1}\) (-0.96 eV) \[45\] and thus displaces phosphorus by site competition. Consequently any reduction in carbon activity has the attendant effect of increasing the phosphorus boundary coverage. The carbide-forming elements chromium, molybdenum, vanadium and niobium do act to decrease the activity of carbon by reducing its solubility and removing it from solution. The underlying nature of the mechanism by which redistribution of the three solutes chromium, molybdenum and phosphorus occurs during purely thermal ageing is of importance for the later discussion of radiation effects.

When the results from this work are analysed in more detail it is seen that there is a particularly strong correlation between the concentrations of phosphorus and the two metallic solutes chromium and molybdenum detected at the boundary planes of the aged material. Figure 5.1(i) shows the strong positive correlation between the chromium and phosphorus concentrations at prior austenite grain boundaries in FV448 aged at 400°C. Each data point represents the detected concentration of both solutes at the plane of each grain boundary analysed. Figures 5.1(ii), (iii) and (iv) are the respective correlations between the two solutes at lath boundaries in material aged at 400°C and at prior austenite and lath boundaries in material aged at 465°C. Similar correlations for detected molybdenum and phosphorus concentrations are shown in Figure 5.2(i)-(iv) for the four permutations of boundary type and ageing temperature. In general, the correlation between the boundary concentrations of both pairs of solute is stronger at the higher
Figure 5.1: Correlations between chromium / phosphorus boundary plane concentrations detected in aged FV448: (i) PAGB's, 400°C, (ii) Lath b.'s, 400°C, (iii) PAGB's 465°C and (iv) Lath b.'s 465°C.
Figure 5.2: Correlations between molybdenum / phosphorus boundary plane concentrations detected in aged FV448: (i) PAGB's, 400°C, (ii) Lath b.'s, 400°C, (iii) PAGB's, 465°C and (iv) Lath b.'s, 465°C.
Figure 5.3: Correlation of chromium/phosphorus and molybdenum/phosphorus concentrations detected at prior austenite and lath boundary planes in FV448 aged at 400° and 465°C.
ageing temperature, and at prior austenite grain boundaries compared with lath boundaries. Figure 5.3 draws together all the data displayed above to show the combined chromium / phosphorus and molybdenum / phosphorus correlations for the four permutations of boundary type and ageing temperature. There is clearly a very strong correlation between the concentration of both these solutes and phosphorus detected at boundary planes in aged FV448, such that for a boundary plane exhibiting enrichment of any one of these solutes there was found to be a corresponding enrichment of both the other two at the same boundary plane. The strength of the correlation between the boundary concentrations of metallic solute and phosphorus decreased in the order: Mo \( (r = 0.96) \), Cr \( (r = 0.87) \), Mn \( (r = 0.58) \) and Ni \( (r = 0.43) \).

Despite the strong evidence here that the three solutes phosphorus, chromium and molybdenum are found to be segregated together, it is difficult to determine unequivocally whether in fact the three are participating in interactive cosegregation, or whether their enrichment is the result of the removal or otherwise of carbon from boundary planes. From the literature, the interactive cosegregation mechanism has been proposed primarily by earlier workers investigating boundary chemistry and embrittlement phenomena in steels - that is, iron alloys with significant carbon contents. The proponents of site competitive action tend to be more recent workers examining the effects of composition in a series of alloys containing the solutes of interest both in low carbon and decarburized variants, thus allowing the role of carbon to become clear [47-49]. The material in this work, FV448, is a commercial grade steel; a multi-component alloy, having a nominal carbon content of 0.1%. Thus it is likely that the interactions of the surface active carbon with the other solutes will play an important part in determining the grain boundary chemistry of this material. Whilst the HB501 FEGSTEM is equipped with a windowless EDX detector, and is thus able to detect X-ray signals down to an energy including that of carbon K\textsubscript{a} , it is not possible to provide a quantitative assessment of carbon content. As discussed in Section 3.6.3.2, outlining experimental procedure, the intense electron probe incident on the foil surface tends to polymerize volatile contaminants present to produce a carbon contamination spot on the foil surface which grows with increasing analysis time. This spurious signal obscures any intrinsic signal generated from carbon within the foil itself. Hence, it was not possible to determine whether the boundaries exhibiting the greatest concentrations of phosphorus, chromium and molybdenum were less rich in carbon than those boundaries showing less enrichment of the three solutes.

The observed greater segregation of solutes to boundaries at the higher ageing temperature of 465°C compared with 400°C, despite the equilibrium interfacial concentration of solutes increasing with decreasing temperature, has been rationalized in

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terms of the kinetic approach to equilibrium. The other variable examined was boundary type; for a given ageing temperature it was found that prior austenite grain boundaries became more heavily segregated than did lath boundaries.

Most workers investigating the role of phosphorus and other solutes in temper embrittlement have used Auger electron spectroscopy to determine boundary plane compositions of intergranularly fractured material. Thus the boundaries exposed for analysis are chosen by the fracture path; fracture in temper embrittled martensitic stainless steels invariably follows the path of prior austenite grain boundaries. If the degree of embrittlement, or reduced boundary cohesiveness, is governed by the magnitude of phosphorus segregation to boundary planes, then it would seem that since fracture occurs preferentially along the prior austenite boundaries, these boundary planes must also be more segregated by phosphorus. This inference neglects the possibility that the prior austenite grain boundary network may morphologically offer a lower energy fracture path.

Some workers have specifically investigated the role of boundary type or misorientation on the degree of phosphorus segregation. Ogura et al. [209,210] examined the relationship between grain boundary crystallography and phosphorus segregation in an Ni-Cr steel. The steel was very slowly cooled from the austenitizing temperature through the \( \gamma \rightarrow \alpha \) transformation to give a coarse grained ferritic structure. The analysis of grain boundary phosphorus concentration was performed by a qualitative etching procedure. They found that for misorientations of less than about \( 12^\circ \) the amount of phosphorus segregation was always very small and therefore concluded that phosphorus cannot segregate to boundaries of which the structure is represented by a two dimensional array of lattice dislocations. This is essentially the case for lath boundaries, which are regarded as walls of dislocations. From their results it was suggested that the controlling crystallographic factor determining the amount of phosphorus segregation at high angle boundaries was their atomic coherency, or free volume, which is not directly related to the grain boundary energy.

A quantitative analysis of both high and low angle boundary microchemistry was performed on a 9Cr-1Mo steel by Vatter and Titchmarsh [64] using an HB501 FEGSTEM. They analysed prior austenite and lath boundary planes in material aged at 550°C for 1000 hours, similarly finding enhanced concentrations of chromium, molybdenum and phosphorus. Whilst they did not explicitly state the fact, examination of their experimental data suggests that lath boundaries were less heavily segregated than prior austenite grain boundaries.
If the determining factor in temper embrittlement is the site competitive action between free carbon and phosphorus then one would expect prior austenite grain boundaries to be relatively freer of solid solution carbon than lath boundary planes, in order to explain the greater levels of segregant at prior austenite boundary planes. High resolution autoradiography was used by Prabhu Guankar et al.\textsuperscript{211} to determine the localization of carbon in the microstructure of a tempered martensitic 12\%Cr-0.15\%C steel. They found that subsequent to tempering in the temperature range associated with maximum embrittlement, the solid solution carbon was located preferentially along the martensitic lath interfaces and the prior austenitic interfaces were correspondingly depleted.

Militzer and Wieting\textsuperscript{37} have proposed a model to account for this effect, involving demixing of carbon and phosphorus at grain boundaries arising from a miscibility gap in the Fe-C-P system, to form metastable phosphorus- and carbon-rich 'phases' at the boundary planes. They argue that if demixing occurs the otherwise insignificantly higher free energy of segregation to prior austenite grain boundaries is sufficient to locate the phosphorus-rich precipitation there. Consequently, the carbon-rich 'phase' is preferentially located at new ferrite boundaries. The degree of coverage of prior austenite grain boundaries by the phosphorus-rich phase is expected to be dependent on the ratio of new ferrite boundary area to existing austenite boundary area; the coverage being greater with a higher proportion of newly formed boundaries. Thus a tempered martensite structure, with its very high proportion of martensite lath boundaries to prior austenite boundaries would be expected to show significant coverage of the austenite boundaries by the phosphorus-rich phase, following their arguments.

\subsection{Electron probe / segregant interaction: model}

One of the characteristics of equilibrium segregation is its spatial distribution; it is confined only to the monolayer immediately adjacent to the boundary plane. The widths of the segregated layers in the aged material, as measured by the full width half maxima of the profiles generated by the FEGSTEM, were 3 to 4 nm. Though narrow, this width is clearly greater than the width of one monolayer either side of a disordered boundary region. This arises because of the finite width of the incident electron probe. If the segregant is truly the result of equilibrium segregation then the total width of the enriched zone will be less than 1 nm. In comparison to this, the electron probe diameter of the Harwell HB501 for typical EDX conditions has been estimated at 3.5 nm, as that diameter containing 80\% of the probe current.

As a consequence, the width of the effect to be measured is less than the width of the measuring device. The acquired solute profile is thus the convolution of the segregant
and electron probe current distributions, where the composition at any point in the profile is the value averaged over the volume of the material excited by the incident electron beam. Hence not only is the apparent width of a segregant distribution altered, but so too is its apparent maximum. The use of a finite probe size smooths out a discontinuous solute distribution; the greater the probe diameter, the more the true distribution becomes smoothed.

Attempts to quantify and deconvolute the true solute distribution from an acquired concentration profile can be approached in two ways. The first method is to convolute an assumed incident electron probe current distribution with an assumed segregant distribution and neglect beam broadening effects caused by high angle elastic scattering of electrons as they negotiate the thin foil. The second method is to incorporate the segregant and electron probe current distributions into a numerical Monte-Carlo simulation which models the beam broadening events in thicker foils.

To actually deconvolute accurately the segregant distribution from the generated profile requires a precise knowledge of the probe current distribution, a large number of closely spaced analysis points across the interface and, for the application of a Monte-Carlo simulation, explicit knowledge of the local foil thickness.

The first method described above, the simple convolution of the two distributions neglecting beam broadening effects will provide a measure of the best profile that could be generated by the geometric interaction of electron probe and segregant distributions. The interfaces analysed in this study were partly chosen as being sited in very thin areas of the foil, where beam broadening effects may not be significant. Thus the first approach is applied here to model analytically the interaction; if beam broadening is significant it will show in the results from the modelling.

The geometry of the interaction is modelled as shown in Figure 5.4. The electron probe current is assumed to be radially normally distributed, with a mean of zero [i.e. centred on (0,0)] and a variance given by $\sigma^2$. The beam intensity at a point $(x,y)$ from the beam centre is then given by:

$$ I = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x^2 + y^2)}{2\sigma^2}\right) $$
Concentration

Distance

\[ I = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x^2 + y^2)}{2\sigma^2}\right) \]

Concentration

Distance

Figure 5.4: Geometry of the electron probe/segregant interaction assumed for analytical modelling; the electron beam distribution is Gaussian, the slab segregant has a concentration profile of the form shown in either (i) or (ii).

\[ C = C_0 + m \left( x - \left( x_d + \frac{1}{2} d_0 \right) \right) \]
The proportion of the total number of electrons incident on a segregated layer of width $d_0$ whose midpoint is a distance $x_d$ from the incident electron probe centre is thus given by:

\[
\frac{\int_{-\infty}^{\infty} \int_{x_d-d_0}^{x_d+d_0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] \, dx \, dy}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] \, dx \, dy}
\]

Evaluating the denominator:

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] \, dx \, dy
\]

\[
= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2\sigma^2}\right) \, dx \, \int_{-\infty}^{\infty} \exp\left(-\frac{y^2}{2\sigma^2}\right) \, dy
\]

\[
= \frac{1}{\sigma\sqrt{2\pi}} \cdot \sqrt{2\pi\sigma^2} \cdot \sqrt{2\pi\sigma^2}
\]

\[
= \sigma\sqrt{2\pi}
\]

Evaluating the numerator:

\[
\int_{-\infty}^{\infty} \int_{x_d-d_0}^{x_d+d_0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] \, dx \, dy
\]

\[
= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp\left(-\frac{y^2}{2\sigma^2}\right) \, dy \int_{x_d-d_0}^{x_d+d_0} \exp\left(-\frac{x^2}{2\sigma^2}\right) \, dx
\]

\[
= \frac{1}{\sigma\sqrt{2\pi}} \cdot 2 \cdot \frac{1}{\sqrt{2\pi\sigma^2}} \int_{x_d-d_0}^{x_d+d_0} \exp\left(-\frac{x^2}{2\sigma^2}\right) \, dx
\]

\[
= \int_{0}^{\infty} \exp\left(-\frac{x^2}{2\sigma^2}\right) \, dx - \int_{0}^{-\infty} \exp\left(-\frac{x^2}{2\sigma^2}\right) \, dx
\]

\[
= \frac{\sigma\sqrt{2\pi}}{2} \left[ \text{erf}\left(\frac{x_d + \frac{d_0}{2}}{\sigma\sqrt{2}}\right) - \text{erf}\left(\frac{x_d - \frac{d_0}{2}}{\sigma\sqrt{2}}\right) \right]
\]
Thus the proportion of the total number of electrons incident on a layer of width $d_0$ situated a distance $x_d$ from the beam centre is:

$$\frac{1}{2} \left[ \text{erf}\left(\frac{x_d + \frac{1}{2}d_0}{\sqrt{2}\sigma}\right) - \text{erf}\left(\frac{x_d - \frac{1}{2}d_0}{\sqrt{2}\sigma}\right) \right]$$

For a solute distribution shown by (i) in Figure 5.4, of a concentration $C_b$ in the segregant layer and $C_0$ in the adjacent matrix, the derived concentration, $C$, generated from an electron probe incident at a distance $x_d$ from a segregant layer of width $d_0$ is thus:

$$C = C_0 + \frac{1}{2}(C_b - C_0) \left[ \text{erf}\left(\frac{x_d + \frac{1}{2}d_0}{\sqrt{2}\sigma}\right) - \text{erf}\left(\frac{x_d - \frac{1}{2}d_0}{\sqrt{2}\sigma}\right) \right] \quad \text{Eqn.}(1)$$

For a fixed width of segregated layer, the derived concentration profile is determined by the standard deviation of the probe distribution, $\sigma$. The probe diameter is usually defined in terms of a diameter containing a certain proportion of the total probe current, usually 80%. Thus we need to find the correspondence between the beam diameter containing, say, 80% of the current and the standard deviation of the normal approximation to the electron distribution.

The electron distribution can be written equivalently in terms of radial coordinates as follows:

$$I = \frac{1}{\sigma \sqrt{2\pi}} \int_0^{2\pi} \int_0^{\infty} \exp \left(\frac{-r^2}{2\sigma^2}\right) r \, dr \, d\theta$$

$$= \frac{1}{\sigma \sqrt{2\pi}} \int_0^{2\pi} d\theta \int_0^{\infty} \exp \left(\frac{-r^2}{2\sigma^2}\right) r \, dr$$

$$= \frac{\sqrt{2\pi}}{\sigma} \left[ -\sigma^2 \exp \left(\frac{-r^2}{2\sigma^2}\right) \right]_0^{\infty}$$

$$= \sigma \sqrt{2\pi}$$
The radius, \( r_{80} \), containing 80\% of the current, \( I_{80} \), is solved by:

\[
I_{80} = 0.8 \sigma \sqrt{2\pi} = \int_0^{2\pi} \int_0^{r_{80}} \exp\left(-\frac{r^2}{2\sigma^2}\right) r \, dr \, d\theta
\]

\[
= \frac{\sqrt{2\pi}}{\sigma} \left[-\sigma^2 \exp\left(-\frac{r_{80}^2}{2\sigma^2}\right)\right]_0^{r_{80}}
\]

\[
\therefore 0.8 = \exp\left(-\frac{r_{80}^2}{2\sigma^2}\right) - 1
\]

\[
\therefore \ln 0.2 = -\frac{r_{80}^2}{2\sigma^2}
\]

\[
\Rightarrow r_{80} = 1.794\sigma
\]

Thus for a beam diameter specified by \( \phi_{80} \), the standard deviation defining the normal approximation to the electron distribution is given by:

\[
\sigma = 0.279 \phi_{80} \quad \text{Eqn.}(2)
\]

5.1.2.2 Electron probe / segregant interaction: data analysis

Now equation (1) can be used in conjunction with the conversion defined by equation (2) to model analytically what the derived concentration profile will be for a given segregant distribution and incident beam diameter. For a matrix concentration of solute \( C_0 = 0.0\% \), a boundary concentration \( C_b = 3.0\% \), a segregant layer width of 1 nm and a nominal beam diameter of 3.5 nm to model the situation for monolayer phosphorus segregation in FV448 analysed by the HB501, the analytically derived concentration profile is as shown in Figure 5.5. The mean data obtained experimentally from prior austenite grain boundaries of material aged at 465°C is also plotted for comparison. It can be seen that whilst the derived profile has been fitted to the maximum of phosphorus concentration detected at the interface, the apparent width of the derived profile is narrower than that observed experimentally. This indicates that one or more of the assumptions made concerning the two distributions are not strictly valid.

Firstly, the segregant was assumed to be a top-hat function of width 1 nm to approximate monolayer segregation either side of a disordered boundary plane. The segregant may extend to greater than one monolayer either side of the interfacial plane, and if so it is likely to have considerable concentration gradient 'tails' rather than be purely a top-hat profile of an adsorbed layer. Secondly, and more likely, the electron probe diameter may effectively be greater than 3.5 nm. Even if the nominal incident beam diameter is 3.5 nm, beam broadening effects may not be negligible, the boundary may not be perfectly
Figure 5.5: Fitting of experimental data for mean phosphorus concentration across prior austenite grain boundaries in FV448 aged at 465°C by theoretical convolutions of monolayer-type segregation with electron probe diameters of (i) 3.5 nm and (ii) 5.4 nm.
aligned with the electron beam and some specimen drift may occur. Each of these factors may contribute to make the effective probe size greater than the nominal incident beam diameter.

If the segregant distribution, a top-hat function of width 1 nm, is assumed to be valid, but now the derived concentration profile is fitted to match the experimentally determined values by altering the probe diameter for the model, the second curve in Figure 5.5 is obtained. Here the effective probe size is increased to 5.4 nm and the boundary concentration of segregant, \( C_b \), is correspondingly increased to 4.5%.

An indication as to whether the effective probe diameter is an accurate assessment of the physical situation can be gained by applying the analytical model to the experimentally determined data for other solutes. The effective probe diameter should remain constant for each solute since the effects of boundary tilt, specimen drift and beam broadening affect the acquisition of the whole X-ray spectrum. The derived concentration profiles modelling the segregation of molybdenum are shown in Figure 5.6. The first profile is derived assuming a beam diameter of 3.5 nm and a 1 nm wide boundary concentration, \( C_b' \), of 30.85%. In this case also, it is too narrow to fit the experimental data for prior austenite grain boundaries in material aged at 465°C. The second profile is obtained using an effective probe size of 5.4 nm and a boundary concentration of 46%, i.e. 0.46 monolayer coverage. The experimental data is matched very well by the analytically derived concentration profile using the same effective probe diameter as for phosphorus above. This consistency suggests that the analytical model is describing the physical situation accurately, but that the incident electron beam diameter is effectively slightly 'broadened' in its interaction with the specimens.

Thus, the apparent grain boundary enrichment detected in the aged FV448 material is consistent with it being the result of equilibrium segregation. Theory suggests that for the ageing times and temperatures of this study, greater segregation should be observed in the material aged at 465°C, despite equilibrium values of interfacial solute concentration increasing with decreasing temperature. The relative magnitudes of equilibrium segregation predicted and experimentally determined are similar for both ageing temperatures. The discrepancy in absolute values is accounted for by the electron probe / specimen interaction. Theoretical calculations regarding the equilibrium segregation of phosphorus in isolation, without the interactions of other solutes, predict a monolayer coverage of 9.8 at.% at grain boundaries in equilibrium at 465°C. The detected value of 1.16 wt.% is the concentration averaged over the interaction volume of the electron probe. Using a convolution of a Gaussian-shaped electron distribution and a top-hat function solute concentration profile of width 1 nm to fit the experimentally determined
Figure 5.6: Fitting of experimental data for mean molybdenum concentration across prior austenite grain boundaries in FV448 aged at 465°C by theoretical convolutions of monolayer-type segregation with electron probe diameters of (i) 3.5nm and (ii) 5.4nm.
data yields a monolayer coverage of 4.5 wt.%. Assuming all the solute enrichment to lie in the 1 nm segregant width, this translates to a phosphorus concentration of 13 at.\%: the boundary plane composition being then approximately (wt.\%): 30Mo-25Cr-16Si-13P-5Mn 4Ni-bal. Fe.

It is interesting to compare this 'deconvoluted' boundary plane composition with the composition of Laves phase reported by Stoter and Little\cite{60} for this steel observed on ageing at 600°C. They gave the composition as (at.\%): 42Fe-25Mo-16Cr-10Si-4P-1.5Mn-1.5Ni. The 'deconvoluted' boundary plane composition detected here is close to the composition of Laves phase with very similar relative magnitudes of solute concentration. It was noted above that although no apparent Laves phase was observed, the ageing temperature of 465°C was very close to the lower limit for Laves phase formation. The boundary regions analysed were deliberately chosen to be free from apparent precipitation, but it is clear from the above analysis that the prior austenite interfaces of FV448 aged at 465°C comprise a collection of solute atoms in similar concentrations to Laves phase: a precursor to its actual nucleation and growth.

5.1.2.3 Irradiated material

The grain boundary microchemistry of the fast neutron irradiated FV448 is subject to modification by the combination of thermal and irradiation effects. The thermal effects have been discussed above for the thermally aged material. The anticipated radiation-induced segregation effects will be discussed and compared with the observed net irradiation effects. Then the combination of thermal and irradiation effects on the gross boundary microchemistry and microstructure of the irradiated material will be discussed.

5.1.2.3.1 Anticipated radiation-induced segregation

The two mechanisms by which radiation induced-segregation is thought to occur have been reviewed in Section 2.3, providing two rules for predicting the direction of solute segregation under irradiation. Firstly, that undersized solutes become enriched and oversized solutes become depleted at point defect sinks. Secondly, that faster diffusing solute species become depleted, whilst slower diffusing species become enriched at solute sinks. The first rule is expected to be more important for dilute solutes and at lower temperatures; the second for concentrated solutes and at relatively higher temperatures.

Each of the solutes present in FV448 whose distribution across interfaces has been accurately determined (namely Cr, Ni, Si, Mo, Mn and P) are analysed below with
respect to iron in the light of the two criteria above. The misfit parameters for the six solutes in iron are given in Table 14, as calculated by King [212] and Kornblit and Ignatiev [213]. The atomic volume misfit factors calculated by King are based upon the change in solvent lattice parameter that the solute exerts. The parameter defined by Kornblit and Ignatiev is based on the ratio of the solute to solvent metallic radii and overcomes certain solute-solvent combinations which apparently break the size effect rule when King's atomic volume misfit parameter is applied. For each of the solutes in this case, the two definitions yield the same sense of misfit, whilst altering slightly the relative magnitudes.

(i) Chromium

Chromium has a slightly positive size factor misfit with respect to iron: it is slightly oversized. Thus the migrational configuration of interstitial dumbbells is to pass the solute by, as set out in Section 2.3.1.2.4. Binding of an oversized solute to the vacancy flux is a possibility, but the binding energy of even the strongest bound vacancy-solute complexes (approximately 0.3 eV) is not thought to be high enough to enable significant solute-vacancy flux coupling. Since chromium is only slightly oversized, strain energy relief considerations implicate a low solute-vacancy complex binding energy: Faulkner [109] has calculated the binding energy of such a complex to be just 0.03 eV.

Chromium is a faster diffusing species than iron in a ferritic matrix from thermal diffusion data [214, 215], i.e. diffusion via vacancy exchange. Hence the preferential exchange of vacancies with chromium en route to point defect sinks will cause an opposite net flux of chromium atoms from the sink region. Since chromium is present as a concentrated solute it is probable that this mechanism will dominate the redistribution of chromium during irradiation. In any event, both mechanisms of radiation-induced segregation would be expected to lead to a depletion of chromium at point defect sinks.

(ii) Nickel

Nickel is also a slightly oversized solute in a ferritic iron matrix and thus from purely strain relief considerations, is unlikely to couple strongly with either the radiation-induced interstitial or vacancy fluxes toward point defect sinks. Muon spin rotation measurements by Möslang et al [216] have provided a value of 0.21 eV for the nickel-vacancy binding energy, which is significantly higher than the approximately 0.03 eV predicted by Faulkner [109], whilst values as high as 1.0 eV for the nickel-interstitial complex binding energy have been assumed for modelling [149]
### Table 14

Atomic volume misfit values for solutes in $\alpha$-iron

<table>
<thead>
<tr>
<th>Element</th>
<th>$r$ (Å)</th>
<th>$\Omega_{sf}$ (%)</th>
<th>$(r_{sol} / r_{solv})^3 - 1$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.24115</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>1.2490</td>
<td>+4.4</td>
<td>+1.9</td>
</tr>
<tr>
<td>Ni</td>
<td>1.2458</td>
<td>+4.9</td>
<td>+1.1</td>
</tr>
<tr>
<td>Si</td>
<td>1.17585</td>
<td>-7.9</td>
<td>-15.0</td>
</tr>
<tr>
<td>Mn</td>
<td>1.36555</td>
<td>+4.9</td>
<td>+33.2</td>
</tr>
<tr>
<td>Mo</td>
<td>1.36255</td>
<td>+27.5</td>
<td>+32.3</td>
</tr>
<tr>
<td>P</td>
<td>1.09</td>
<td>-13.2</td>
<td>-32.3</td>
</tr>
</tbody>
</table>

Misfit parameters:

- $\Omega_{sf}$: King [212]
- $(r_{sol} / r_{solv})^3 - 1$: Kornblit and Ignatiev [213]
The diffusion data for nickel in ferritic iron is contradictory. A review of data presented by Fridberg et al [214] suggests that the diffusivity of nickel in ferrite is lower than the self-diffusivity of iron. In contrast, a more recent review by Kucera and Stransky [215], but using similarly aged data, shows nickel to be a faster diffusing species than the host iron atoms.

It is thus unclear from the above as to which direction nickel would tend to segregate under the action of persistent point defect fluxes. Since nickel is present as a dilute solute and the diffusion data suggests that the diffusivity of nickel is little different from that of the host, the inverse Kirkendall effect is not likely to be the significant redistribution mechanism. Any coupling between nickel atoms and either species of point defect would lead to enrichment of nickel at point defect sinks.

(iii) Silicon

Silicon is an undersized substitutional solute in a ferritic iron matrix. As such, strong binding to form mixed dumbbell interstitial complexes with self-interstitials is likely. The observations by Adetunji [58] of quench-induced non-equilibrium segregation of silicon to boundaries in DIN 1.4914 also imply the formation and subsequent migration of coupled silicon-vacancy complexes in iron. Faulkner's calculations of the silicon-vacancy binding energy yield a value of 0.2 eV [109].

Silicon atoms diffuse faster than iron atoms in a ferritic iron matrix [214,215]. Hence, if the vacancy-induced Kirkendall effect was the dominant mechanism, silicon depletion at vacancy sinks may be expected. However, the strong binding between silicon and either point defect flux is more likely to generate enrichment of silicon at point defect sinks.

(iv) Manganese

Manganese is an oversized solute in ferritic iron and is a faster diffusing species [214,215] than the host atoms. Therefore analogous arguments to those for the migration of chromium apply: both mechanisms of radiation-induced segregation would lead to a depletion of manganese at point defect sinks.

(v) Molybdenum

As with chromium and manganese, molybdenum is oversized in a ferritic iron matrix and is a faster diffusing species [214,215]. However, molybdenum is markedly oversized and consequently is more likely to form migrating vacancy-solute complexes. Evidence for this comes from Adetunji's [58] observations of molybdenum segregation at boundaries in
DIN 1.4914 via quench-induced vacancy-coupled non-equilibrium segregation. The binding energy of such complexes has been calculated at 0.3 eV by Faulkner [109]. Thus while both the size effect rule and diffusion rate rule predict molybdenum depletion, coupling to the vacancy flux and consequent solute enrichment at point defect sinks cannot be discounted.

(vi) Phosphorus

Phosphorus is a significantly undersized solute in ferritic iron and is therefore expected to form mixed dumbbell interstitial complexes in iron, thereby becoming enriched at point defect sinks. However, phosphorus is also a much faster diffusing species in iron than the iron atoms themselves [214]; thus if the vacancy-induced inverse Kirkendall effect was dominant, phosphorus depletion at vacancy sinks may be expected. The extremely low concentration of phosphorus makes this possibility unlikely, with strong binding to the interstitial flux the more probable dominant mechanism.

From the foregoing it is clear that despite the apparent simplicity of the two criteria determining the kinetic interaction of solutes with point defect fluxes, for only two of the solutes - chromium and manganese - is the anticipated direction of any radiation-induced segregation unequivocal.

In addition, it should be emphasized that the above considerations are based on each element being the single solute in an Fe-X binary system. It may be recalled from Section 2.3.3 that experiments involving two individual solutes in nickel binary alloys led to one of the solutes becoming enriched and the other depleted at point defect sinks; incorporation of both solutes to form the corresponding ternary system led to the enrichment of one solute, but not to the depletion of the other relative to the host. The enrichment and depletion in the binary alloys were both a result of the action of the same point defect species. The presence of a sufficient concentration of one solute saturated the point defect flux such that depletion of the other was suppressed. Such competitive action is clearly a distinct possibility in the multi-component alloy under investigation here.

Furthermore, as well as the likelihood of competition between the solutes for interaction with the point-defect fluxes, there is the possibility of synergistic action between solute species. For example, molybdenum and phosphorus are reported to have a strong chemical affinity for each other, with an interaction energy of ~0.4 eV as discussed above for the aged material. It is thus perhaps unrealistic to discuss the migration of each solute.
independently, when the motion of one will clearly influence the next migrational step of the other.

5.1.2.3.2 Observed net irradiation-induced solute redistribution

The principal net irradiation effects of high dose fast neutron irradiation on solute redistribution, relative to aged material at interfaces in FV448 were observed to be: (i) depletion of chromium from near boundary planes, (ii) a reduction in the boundary plane concentration of chromium, molybdenum and phosphorus, (iii) slight apparent nickel enrichment at lath boundaries at both irradiation temperatures, (iv) enrichment of silicon at both boundary types at 400°C irradiation and (v) a possible depletion of manganese concentration towards boundaries. These apparent net radiation-induced effects are discussed for each solute with regard to the anticipated effects set out above.

(i) Chromium

Chromium is the major solute addition to FV448 and is present at a sufficient concentration to be regarded as a concentrated alloy. Since it diffuses faster than the solvent self-diffuses, preferential vacancy exchange will lead to the opposing atomic flux associated with the vacancy flux to be richer in chromium than the local matrix composition: the apparent net depleton of chromium from boundary regions is in accordance with this. The passage by of an interstitial flux to point defect sinks would also lead to a depletion of chromium at the boundary planes, but the gross effect of the irradiation history on the spatial extent of chromium redistribution in relation to other species suggests that this is not the dominant mechanism.

(ii) Nickel

Since nickel is present only as a dilute solute, point defect-solute complex migration is likely to be the dominant mechanism of any radiation-induced segregation. Its observed enrichment at lath boundaries implies significant coupling between nickel atoms and the point defect fluxes, possibly a preferential interaction with the interstitial flux, since lath boundaries are essentially planar arrays of dislocations. Dislocations are sinks preferentially biased towards interstitials [217,218]; so, by extension, might lath boundaries be, but to a lesser extent owing to intersecting stress fields. Faulkner et al [149] have modelled radiation-induced segregation considering only the migration of interstitial-solute complexes as causing solute redistribution. The model suggests that the peak temperature for radiation-induced segregation of nickel in ferritic iron at a damage rate of $1 \times 10^{-6}$ dpa s$^{-1}$ is in the region of 250°C with the magnitude decreasing with increasing temperature above that, Figure 2.36.
(iii) Silicon

As an undersized solute, the observed enrichment of silicon at boundaries following irradiation is in accordance with the anticipated formation and migration of mixed dumbbell interstitial complexes to the boundary planes. The greater degree of enrichment at the lower irradiation temperature of 400°C is in agreement with modelling by Faulkner et al [150], again considering only radiation-induced segregation by the migration of interstitial-solute complexes. The predicted temperature for peak segregation of silicon at a damage rate of $1 \times 10^{-6}$ dpa s$^{-1}$ is about 140°C: at temperatures above this, increasing the irradiation temperature serves to decrease the predicted magnitude of segregation, Figure 2.34.

(iv) Manganese

The observed net depletion of manganese from boundary regions in the irradiated FV448 can be explained by the operation of either manganese preferentially diffusing away through faster vacancy exchange, or through its displacement by other species in the form of self interstitials or mixed dumbbell interstitials.

(v) Molybdenum

From both size effect considerations and diffusion rate arguments, molybdenum is anticipated to become depleted at point defect sinks by radiation-induced segregation. The net irradiation effect was for the molybdenum concentration at boundary planes to be significantly less than found in the aged material: whether this is actually radiation-induced solute depletion or a retardation of thermal effects will be discussed below.

(vi) Phosphorus

Since phosphorus is significantly undersized in ferritic iron, the formation and migration of stable mixed dumbbell interstitials to defect sinks is anticipated to lead to grain boundary enrichment of phosphorus, as modelled by Faulkner et al [150] in Figure 2.35. However, the net effect of irradiation was found to be to cause the interfacial concentrations of phosphorus actually to be less in the irradiated material than in the corresponding thermally aged material. Again, whether this really corresponds to net depletion via radiation-induced segregation will be discussed below.

5.1.2.3.3 Gross behaviour of Cr, Mo and P under irradiation

It is interesting to note that the concentrations of chromium, molybdenum and phosphorus at boundary planes in the fast neutron irradiated FV448 are all reduced in comparison to the thermally aged material. It will be recalled that in the aged material
these three solutes exhibited a very strong correlation between the detected boundary concentrations of each other. Intuitively then, it may not seem surprising that the effect of irradiation will be to alter the redistribution of all three in a similar way. However, this does not necessarily take into account the precise mechanism which causes the three solutes to be segregated at interfaces during thermal ageing.

When discussing the mechanism for the enrichment of these three solutes - equilibrium segregation - it was noted that neither chromium nor molybdenum have an intrinsic segregation free energy to grain boundaries in 12%Cr steels. It was argued that the driving force for their observed enrichment was their strong interaction energies with phosphorus, which is itself highly surface active. Although both chromium and molybdenum were anticipated to become depleted from near to point defect sinks under the action of persistent point defect fluxes, this should not cause the depletion of phosphorus. Firstly, the segregation free energy of phosphorus (47 kJ mol\(^{-1}\), 0.49 eV) is greater than the interaction energies between phosphorus and either chromium (17 kJ mol\(^{-1}\), 0.17 eV) or molybdenum (37.5 kJ mol\(^{-1}\), 0.38 eV). Secondly, chromium in particular is present as a concentrated solute, thus the mean field with respect to chromium surrounding a single phosphorus atom will remain essentially the same. Thirdly, phosphorus itself is anticipated to become enriched at point defect sinks by the action of persistent point defect fluxes, regardless of any thermal effects. Finally, although chromium was found experimentally to become depleted from regions adjacent to boundary planes in the irradiated material, there was a local increase in its concentration such that the detected apparent boundary plane concentration of chromium was approximately equal to that of the initial, as-tempered, material. Owing to the finite electron probe size, the detected composition is the average composition over the volume of probe interaction. Therefore, since the matrix chromium concentration immediately adjacent to the boundary plane is lower than the as-tempered composition, then the true boundary plane chromium concentration in the irradiated material must actually be greater in order that the sampled boundary plane compositions remain approximately equal.

This can be quantified by extending the analytical model for the electron probe / interface interaction to approximate the derived concentration profile for chromium as observed in the irradiated material. The electron beam current is assumed to be radially normally distributed as before. Now, however, the concentration profile is assumed to be of the form shown as (ii) in Figure 5.4. The boundary monolayer has a composition \(C_b\) and thickness \(d_0\) with an adjacent matrix concentration of \(C_0\), but which increases linearly with increasing distance from the interface with a concentration gradient, \(m\), such that:

\[
C = C_0 + m(x - (x_d + \frac{1}{2}d_0))
\]
This approximates the observed depletion of chromium towards the boundary plane. The apparent concentration, averaged over the volume of the foil excited by the electron current distribution at a distance \( x_d \) from the centre of the interface, is given in this case by:

\[
C = \left\{ \int_{-\infty}^{\infty} \int_{-\infty}^{x_d - \frac{1}{2}d_0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] (-m(x - (x_d - \frac{1}{2}d_0)) + C_0) \, dx \, dy 
\right.
\]

\[
+ \int_{-\infty}^{\infty} \int_{x_d + \frac{1}{2}d_0}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] C_b \, dx \, dy 
\]

\[
+ \int_{-\infty}^{\infty} \int_{x_d + \frac{1}{2}d_0}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] \left(m(x - (x_d + \frac{1}{2}d_0)) + C_0\right) \, dx 
\}

\]

\[
/ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x^2 + y^2)}{2\sigma^2}\right] \, dx \, dy
\]

By inspection, the factor \( \int_{-\infty}^{\infty} \exp\left[-\frac{y^2}{2\sigma^2}\right] \, dy \) and the denominator double integral are equal and thus cancel. Hence, the apparent concentration is given by the summation of the three integrals:

\[
C = \int_{-\infty}^{x_d - \frac{1}{2}d_0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] (-m(x - (x_d - \frac{1}{2}d_0)) + C_0) \, dx 
\]

\[
+ \int_{x_d + \frac{1}{2}d_0}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] C_b \, dx 
\]

\[
+ \int_{x_d + \frac{1}{2}d_0}^{\infty} \frac{1}{\sigma\sqrt{2\sigma}} \exp\left[-\frac{x^2}{2\sigma^2}\right] \left(m(x - (x_d + \frac{1}{2}d_0)) + C_0\right) \, dx 
\]
Evaluating the three integrals separately:

(i) 
\[
\int_{-\infty}^{x_d - \frac{1}{2}d_0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] (-m(x - (x_d - \frac{1}{2}d_0)) + C_0) \, dx
\]
\[
= \int_{-\infty}^{x_d - \frac{1}{2}d_0} \frac{-mx}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] \, dx + \int_{x_d - \frac{1}{2}d_0}^{x_d} \frac{C_0 + m(x_d - \frac{1}{2}d_0)}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] \, dx
\]
\[
= \left[ \frac{m\sigma}{\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right]\right]_{-\infty}^{x_d - \frac{1}{2}d_0} + \left\{ \frac{C_0 + m(x_d - \frac{1}{2}d_0)}{2} \left( 1 + \text{erf}\left[\frac{x_d - \frac{1}{2}d_0}{\sigma\sqrt{2}}\right]\right) \right\}
\]
\[
= \frac{m\sigma}{\sqrt{2\pi}} \exp\left[-\frac{(x_d - \frac{1}{2}d_0)^2}{2\sigma^2}\right] + \frac{C_0 + m(x_d - \frac{1}{2}d_0)}{2} + \text{erf}\left(\frac{x_d - \frac{1}{2}d_0}{\sigma\sqrt{2}}\right) \cdot \frac{C_0 + m(x_d - \frac{1}{2}d_0)}{2}
\]

(ii) 
\[
\int_{x_d - \frac{1}{2}d_0}^{x_d + \frac{1}{2}d_0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] C_b \, dx
\]
\[
= \int_{0}^{x_d + \frac{1}{2}d_0} \frac{C_b}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] \, dx - \int_{0}^{x_d - \frac{1}{2}d_0} \frac{C_b}{\sigma\sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma^2}\right] \, dx
\]
\[
= \frac{C_b}{2} \left[ \text{erf}\left(\frac{x_d + \frac{1}{2}d_0}{\sigma\sqrt{2}}\right) - \text{erf}\left(\frac{x_d - \frac{1}{2}d_0}{\sigma\sqrt{2}}\right) \right]
\]

(iii)
Thus, summing the integrals, Eqn.(3):

\[
\int_{x_d + \frac{1}{2}d_0}^{\infty} \frac{1}{\sigma \sqrt{2\pi}} \exp\left[\frac{-x^2}{2\sigma^2}\right] (m(x - (x_d + \frac{1}{2}d_0)) + C_0) \, dx
\]

\[
= \int_{x_d + \frac{1}{2}d_0}^{\infty} \frac{m}{\sigma \sqrt{2\pi}} \exp\left[\frac{-x^2}{2\sigma^2}\right] dx + \int_{x_d + \frac{1}{2}d_0}^{\infty} \frac{C_0 - m(x_d + \frac{1}{2}d_0)}{\sigma \sqrt{2\pi}} \exp\left[\frac{-x^2}{2\sigma^2}\right] dx
\]

\[
= \left[\frac{-m \sigma}{\sqrt{2\pi}} \exp\left[\frac{-x^2}{2\sigma^2}\right]\right]_{x_d + \frac{1}{2}d_0}^{\infty} + \left\{\frac{C_0 - m(x_d + \frac{1}{2}d_0)}{2}\left(1 - \text{erf}\left(\frac{x_d + \frac{1}{2}d_0}{\sigma \sqrt{2}}\right)\right)\right\}
\]

\[
= \frac{m \sigma}{\sqrt{2\pi}} \exp\left[\frac{-(x_d + \frac{1}{2}d_0)^2}{2\sigma^2}\right] + \frac{C_0 - m(x_d + \frac{1}{2}d_0)}{2} \cdot \text{erf}\left(\frac{x_d + \frac{1}{2}d_0}{\sigma \sqrt{2}}\right) \cdot \left[\frac{C_0 - m(x_d + \frac{1}{2}d_0)}{2}\right]
\]

Thus, summing the integrals, Eqn.(3):

\[
C = C_0 - \frac{m d_0}{2} + \frac{m \sigma}{\sqrt{2\pi}} \left[\exp\left(\frac{-(x_d + \frac{1}{2}d_0)^2}{2\sigma^2}\right) + \exp\left(\frac{-(x_d - \frac{1}{2}d_0)^2}{2\sigma^2}\right)\right]
\]

\[
+ \text{erf}\left(\frac{x_d - \frac{1}{2}d_0}{\sigma \sqrt{2}}\right) \cdot \left[\frac{C_0 - C_b + m(x_d - \frac{1}{2}d_0)}{2}\right] - \text{erf}\left(\frac{x_d + \frac{1}{2}d_0}{\sigma \sqrt{2}}\right) \cdot \left[\frac{C_0 - C_b + m(x_d + \frac{1}{2}d_0)}{2}\right]
\]

When the concentration gradient is zero, i.e. \(m = 0\)

\[
C = C_0 + \frac{1}{2} (C_b - C_0) \cdot \left[\text{erf}\left(\frac{x_d + \frac{1}{2}d_0}{\sigma \sqrt{2}}\right) - \text{erf}\left(\frac{x_d - \frac{1}{2}d_0}{\sigma \sqrt{2}}\right)\right] \text{ as previously, Eqn.(1)}
\]

If this analytically derived concentration profile, equation (3), is now fitted to an experimentally determined profile, a measure of the boundary concentration, \(C_b\), can be obtained. The effective beam diameter is taken to be 5.4 nm and the width of the segregated layer 1 nm, as before. The best fit to the mean experimental data from lath boundaries in FV448 irradiated at 400°C is obtained when \(C_b = 13.3\%\), \(C_0 = 9.85\%\) and \(m = 0.013\) nm\(^{-1}\). The analytically derived profile and the experimental data are shown in Figure 5.7. Thus the value determined to be a measure of the true boundary concentration, 13.3\%, is actually greater than the uniform chromium concentration, of 11.1\% detected across lath boundaries in the as-tempered condition. This boundary plane enrichment is in spite of chromium being depleted from regions adjacent to the boundary plane.
Figure 5.7: Fitting of experimental data for mean chromium concentration across lath boundaries in FV448 irradiated at 400°C by the theoretical convolution of a solute distribution as shown in Figure 5.4 (ii) with a gaussian electron probe of 5.4nm diameter.
The observed behaviour of chromium, then, is the result of at least two of the five possible mechanisms influencing interfacial microchemistry set out in Section 2.2.2. Radiation-induced segregation depletes chromium from grain boundary regions whilst superimposed upon this is a Gibbsian adsorption or equilibrium segregation effect. The situation is analogous to that illustrated in Figure 2.20 where a solute is preferentially removed from an interface by sputtering, yet locally there is still a driving force for Gibbsian adsorption by minimization of strain energy. The absolute magnitude of the interfacial concentration is reduced, but its enrichment relative to the local matrix concentration remains similar.

In order to aid comparison, the corresponding mean experimental data from lath boundaries of material aged at 400°C, has been fitted with an analytically derived concentration profile to determine a measure of the boundary concentration, \( C_b \). Again a segregant layer width of 1 nm and an effective beam diameter of 5.4 nm are assumed for consistency. The best fit to the data is shown in Figure 5.8, obtained for values of \( C_b = 17\% \), \( C_0 = 10.8\% \) and a concentration gradient of zero.

Therefore, although there is a deduced enrichment of chromium at boundaries in fast neutron irradiated FV448 to above the initial as-tempered composition, the enrichment is less both in absolute magnitude compared with the corresponding thermally aged condition, and also relative to the immediately adjacent matrix composition.

The reduction in boundary plane phosphorus concentration detected in the irradiated FV448 compared with the thermally aged material was quite unexpected. Convoluting the assumed electron probe current distribution having an effective diameter of 5.4 nm with a top-hat function representing the segregant distribution to fit the experimental data from prior austenite grain boundaries in 465°C irradiated FV448 yields a predicted boundary layer coverage of 1.3 wt.%. This translates to 4.3 at.%, compared with the 13.7 at.% boundary layer coverage deduced from experimental data obtained from prior austenite boundaries of the material thermally aged at 465°C.

Phosphorus is a significantly undersized solute and would be expected to become incorporated into mixed dumbbell interstitials which diffuse down the irradiation-induced concentration gradient to point defect sinks, thereby leading to the radiation-induced enrichment of phosphorus at such sinks. This anticipated enrichment of phosphorus would be in addition to the Gibbsian adsorption, or equilibrium segregation, that was found in the thermally aged material. Hence the observation that interfaces in the fast neutron irradiated material were actually less enriched in phosphorus than those in the corresponding thermally aged material is both surprising and significant.
Figure 5.8: Fitting of experimental data for mean chromium concentration across lath boundaries in FV448 aged at 400°C by the theoretical convolution of monolayer-type segregation with a gaussian electron probe of 5.4nm diameter.
There may be three possible explanations for this seemingly anomalous behaviour of phosphorus. Firstly, if interactive cosegregation with chromium and molybdenum is responsible for the enrichment of phosphorus at boundaries during ageing, then any tendency for radiation-induced segregation to deplete the oversized solutes chromium and molybdenum from boundaries may result in co-depletion of phosphorus. Secondly, if it is the boundary activity of carbon which governs the enrichment of phosphorus, then any increase in carbon activity under irradiation would restrict phosphorus enrichment by site competition. Finally, since phosphorus is present only as a trace impurity in this commercial grade steel, any radiation-induced precipitation incorporating this element will significantly reduce the amount available for segregation.

The mechanism underlying the first of these explanations has been discussed above for the case of the thermally aged material. The phenomenon of interactive cosegregation has not gained universal acceptance. Moreover, the intrinsic segregation free energies of chromium and molybdenum have both been reported as being negligible [45]; their enrichment arises from the strong affinity which they have for phosphorus, which is itself surface active. Thus, simply because chromium or molybdenum were to move away from interfacial regions, it does not follow that phosphorus will similarly be depleted. In fact, chromium, as shown above, and molybdenum were both still found to become locally enriched at boundary planes after irradiation.

The second explanation relies on the mechanism put forward for equilibrium segregation of phosphorus in alloy steels by sceptics of cosegregation theory. The decrease in carbon activity caused by strong carbide forming elements such as chromium, molybdenum, vanadium and niobium lessens the site competition for boundary sites experienced by phosphorus, prompting its greater boundary coverage. If one effect of neutron irradiation was to increase the carbon activity, phosphorus grain boundary coverage would be lessened by an increase in site competitive action.

The primary effect of energetic particle irradiation on a material is the formation of an excess population of point defects via displacement cascades, as reviewed in Section 2.2. Indeed, it is the motion of these to point defect sinks which lies behind radiation-induced segregation. The presence of an increased concentration of vacancies may increase the apparent solubility of carbon in ferrite. Carbon is found to form stable vacancy-solute complexes with a measured binding energy of 0.41 eV [219]. Trapping of carbon atoms by the increased population of vacancies would cause an apparent reduction in the matrix concentration of dissolved carbon, leading to an effective undersaturation of the matrix with respect to carbon. Carbide dissolution, aided by displacement mixing, would redress this, prompting an increase in carbon activity. Carbide dissolution under
irradiation has been discussed by Pugh [220] and Damask [221] and is observed experimentally [61]. In addition, nickel and silicon are both solutes which cause an increase in carbon activity [222-227]; they too are the solutes observed to segregate to interfaces under irradiation. Thus, their increased presence at boundaries would also serve to raise the activity of carbon. The more surface active carbon would reside preferentially at boundary planes, displacing phosphorus via site competition effects. Any lessening of phosphorus concentration at boundary planes would also prompt a corresponding decrease in affiliated chromium and molybdenum concentrations.

The third possible explanation for the diminished boundary coverage by phosphorus after irradiation, compared with thermal ageing, is the removal of the solute via its incorporation into precipitate phases. This present study detected significant incorporation of phosphorus into the widely distributed phases identified by EDX as M₆X (~1 wt.% P) and G phase (~2.5 wt.% P). The comprehensive analysis of precipitate development in FV448 under fast neutron irradiation by Stoter and Little [60] confirms the incorporation of phosphorus into M₆X. They also reported its inclusion in χ phase (~3 at.% P) present after irradiation at 420 and 460°C and in σ phase (~5 at.% P) present after 420 and 460°C irradiation. Furthermore, they also reported the presence of the phosphide MP following irradiation at 460°C [228]. Precipitation of any of these phases will thus serve to reduce the limited population of phosphorus atoms able to migrate to boundary planes.

One of the effects post-irradiation annealing at 465°C for 1000 hours had on boundary microchemistry was to increase the detected concentration of phosphorus (together with molybdenum and chromium) at interfaces, particularly prior austenite boundaries. The radiation-induced phases incorporating phosphorus, M₆X and G phase, were still evident with no obvious dissolution. Hence, the removal from solution of phosphorus by these precipitates does not seem to be the principal cause of lessened segregation during irradiation, although it must be a contributory factor.

Hence, on the evidence available, the most reasonable explanation for the diminished segregation of phosphorus (and consequently chromium and molybdenum) lies in an increased carbon activity under irradiation providing site competition and a repulsive interaction with phosphorus.

5.1.2.3.4 Gross behaviour of nickel and silicon under irradiation

Both of the phases induced by neutron irradiation are significantly enriched in nickel and silicon in comparison to not only the stable carbide M₂₃C₆, but also the typical
composition of Laves phase which is observed to form during long term ageing of molybdenum-containing 12%Cr steels, Table 5. Since nickel and silicon are present only as dilute solutes (∼0.6%) it does imply that strong radiation-induced segregation of these solutes to defect sinks is occurring, causing local supersaturation. This implication is reinforced by the distribution of the phases, with the striking nucleation of G phase along dislocation lines, Figure 4.84.

However, the measured concentrations of nickel and silicon at interfaces in the irradiated material were just slightly higher that at interfaces in thermally aged material for silicon only at the 400°C treatment temperature, and for nickel only at lath boundaries but at both temperatures. From the ideal composition of the radiation-induced G phase (M₆Ni₁₆Si₇) in particular, it may be expected that nickel and silicon would both be very much more enriched at planar point defect sinks, such as grain and lath boundaries, than they apparently are.

Again, the fact that the detected concentration is the averaged composition of the volume sampled by the incident electron probe, may play a part. The full width half maxima of the nickel and silicon concentration profiles in the irradiated material are no wider than those for the equilibrium segregation of phosphorus in the aged material. This suggests that the widths of the nickel and silicon concentration profiles from the irradiated material are similarly as much a measure of the effective diameter of the incident electron current distribution as the true segregant profile widths.

Although the analytical derivation performed above for the electron probe / segregant convolution assumed monolayer, or equilibrium, segregation and will not be strictly valid for a non-equilibrium solute concentration profile, its qualitative effects remain valid. Thus in the absence of knowing precisely the true shape of the nickel and silicon concentration profiles across the interfaces in irradiated material, this derivation will be used in the analysis of those profiles.

When discussing the derived concentration profiles for chromium, above, it was noted that the apparent solute concentration detected from an electron excited volume of material close to the interface depends on not only the true interface concentration, \( C_b \), but also on the adjacent matrix concentration \( C_0 \). When \( C_0 \) is approximately the same for two conditions any variation in detected boundary plane concentration between the two conditions is directly proportional to the change in actual boundary concentration \( C_b \). But, in the case of nickel and silicon, the matrix concentrations of both solutes in the irradiated material are only approximately 1/3 of the matrix concentrations of the aged material. To have actually detected the same apparent boundary plane concentrations
Figure 5.9: The effect of adjacent matrix concentration, \( C_0 \), on the apparent boundary plane solute concentration for segregants of the same true interfacial concentration; \(- - -\) \( C_b = 5.0 \) wt.\%, \( C_0 = 0.6 \) wt.\%, \(- - - -\) \( C_b = 5.0 \) wt.\%, \( C_0 = 0.2 \) wt.\%. Experimental data, for comparison, is of nickel concentration across prior austenite grain boundaries of FV448 treated at 400°C.
from both conditions would mean that the true boundary plane solute concentration from the irradiated material was, in fact, greater than that from the aged material.

This effect is quantified as follows. Figure 5.9 shows theoretical derived solute concentration profiles for solutes having the same true boundary concentration, $C_b = 5.0\%$, but differing matrix concentrations, of $C_0 = 0.6$ and $C_0 = 0.2\%$ respectively. The assumed geometry is as previously with an effective probe diameter of 5.4 nm and a segregated layer width of 1 nm. The apparent maximum concentration of solute detected at the plane of the boundary is then 1.75\% for a matrix concentration of 0.6\%, but 1.45\% for a matrix concentration of 0.2\%. For comparison, the mean boundary plane concentration of nickel detected at prior austenite boundaries in FV448 aged at 400°C was $1.74 \pm 0.36$ wt.\%, whilst in the material fast neutron irradiated at 400°C it was $1.36 \pm 0.32$ wt.\%. Thus, despite apparently less nickel segregation being detected in the irradiated material, the measured concentrations are actually consistent with the same true boundary concentrations in both cases. A further point to this is that even though the boundary concentrations may be similar following both treatments, the enrichment ratio $C_b/C_0$ is a factor of three greater in the irradiated material by virtue of the reduction in matrix concentration from 0.6 to 0.2\%. Considering now the case of lath boundaries in material treated at 465°C, where net enrichment was detected following irradiation notwithstanding the effect of the probe segregant convolution. A detected boundary concentration of $1.48 \pm 0.23\%$ in the irradiated material implies a true boundary concentration of approximately 5.1\%, whilst a true boundary concentration of 3.25\% is inferred from a detected boundary concentration of $1.29 \pm 0.06\%$ in the thermally aged material. These figures correspond to an enrichment factor of 26 in the case of the irradiated material, but just 5.4 for the aged material.

5.2 Weld zone material

5.2.1 Microstructure

5.2.1.1 As-tempered condition

The structure of the as-tempered weld material shows features typical of the high temperatures and steep temperature gradients induced during the welding process. The higher temperatures achieved in the solid state region of the weld zone allow the formation of $\delta$-ferrite and its subsequent retention on rapid cooling. The microstructure of a stainless steel weld pool is dependent upon the solidification mode and transformation effects on cooling. The composition of the weld pool was altered by the use of PE16 filler material, leading to a mean weld pool composition of (wt.\%): 13.3Cr-4.7Ni-0.8Mn-0.8Mo-0.5Si-0.3Nb-0.1V-bal.Fe. The corresponding chromium and
nickel equivalents, as defined in Section 2.1.2, are \( \text{Cr}_{\text{eq}} = 16.5 \) and \( \text{Ni}_{\text{eq}} = 5.1 + 30 \times \text{wt.}\% \text{ C} \). The nickel equivalent is strongly dependent upon the carbon content of the weld pool. The nominal carbon content of the parent plate was 0.1\% C. Dependent upon the extent, if any, of decarburization during the welding process, the nickel equivalent lies between 5.1 and 8.1.

Reference to the liquidus and solidus projections for the ternary Fe-Cr-Ni system \(^{229}\) reveals that, for such compositions, cooling proceeds via primary ferritic solidification with subsequent transformation to austenite. Further transformation of austenite to martensite occurs during the rapid cooling provided by the argon quench. The \( M_s \) and \( M_f \) temperatures for the FV448 parent plate were given as 325\(^\circ\)C and 140\(^\circ\)C respectively, see Table 2. The extra solute concentration in the weld pool will tend to depress these martensitic transformation temperatures. The effects of solute additions on the \( M_s \) temperature of 12%Cr steels were given in Section 2.1.2: the predicted effect of the additional solute concentration of the weld pool is a depression of \( M_s \) by 105\(^\circ\)C. This estimate disregards any decarburization; carbon has a potent effect on lowering \( M_s \). A carbon concentration of 0.1\% lowers \( M_s \) by 42\(^\circ\)C, thus any reduction in carbon concentration from this level could raise \( M_s \) by up to a corresponding degree. Hence the \( M_s \) temperature of the weld pool is estimated to lie in the range 220\(^\circ\) to 265\(^\circ\)C, and the \( M_f \) temperature in the range 35 to 80\(^\circ\)C. This, taken together with reference to the well known Schaeffler diagram, predicting constituent phases present on cooling from welding based on chromium and nickel equivalents (Figure 2.4), predicts a just fully martensitic structure. This is observed in the as-tempered weld material; coarse packets of lath martensite were found to be strongly oriented in the direction of heat flow.

The change in the \( A_c_1 \) temperature of the fusion zone is of importance for determining the effects of subsequent thermal treatments. Empirical relationships quantifying the effects of solute additions on the \( A_c_1 \) temperature of 12%Cr steels have been determined by Irvine et al \(^{8}\). These predict a lowering of the \( A_c_1 \) transformation temperature of the fusion zone by about 45\(^\circ\)C from the 800\(^\circ\)C of the parent plate. This leads to an estimated \( A_c_1 \) temperature of around 755\(^\circ\)C for the mean composition of the fusion zone material. Post-welding heat treatment consisted of a 6 hour temper at 750\(^\circ\)C; clearly very close to, if not actually above, the temperature at which re-austenitization is estimated to be begin to occur.

Despite the superficially homogeneous lath martensitic structure observed to comprise the fusion zone’s microstructure it was found that solute partitioning effects were superimposed upon the lath structure to give an essentially bimodal solute distribution. That the structure was entirely martensitic was checked by selected area diffraction.
analysis coupled with energy dispersive X-ray analysis to verify the crystal structure of both extremes of solute distribution. The solute partitioning had occurred between the austenite stabilizing elements nickel and manganese on the one hand, and the ferrite stabilizing elements chromium and molybdenum on the other. Compositional profiles within the fusion zone are initially determined by partitioning during solidification, but may be modified by diffusional processes in the solid state during further cooling and subsequent tempering. Brooks et al. [230,231] and Cieslak et al. [232] concluded from EDX studies that during both primary ferritic and primary austenitic solidification nickel is depleted at the cores of the cellular dendrites and is correspondingly enriched in the last remaining liquid. Chromium is enriched at dendrite cores during primary ferritic solidification, but, in common with nickel, is depleted during primary austenitic solidification. The observed partitioning behaviour is hence in accordance with the anticipated primary ferritic solidification mode, transforming to austenite and thence to martensite on further cooling. However, as noted above, the equilibrium structure may also be two phase at the tempering treatment temperature of 750°C which would also lead to solute partitioning between the two phases.

The observed compositional profiles can provide some evidence as to whether the solute partitioning is a remnant of the solidification process, or is caused by the tempering treatment, or indeed is a result of the combination of both. Reference to Figure 4.77 reveals that the regions of relatively higher concentration of ferrite stabilising elements exhibit almost uniform solute concentrations right up to an interface. In contrast, the regions of higher concentrations of austenite stabilizing elements exhibit marked concentration gradients towards the interface.

The mean total diffusion distance of a solute is given by $2\sqrt{Dt}$ where $D$ is the diffusion coefficient and $t$ is the time at temperature. Boothby [233] has calculated diffusion distances as a function of cooling time of a single pass full penetration butt weld on 2.5 mm thick plate using the gas tungsten arc process; the same procedure as used in this work. The results are shown in Figure 5.10. The diffusion distances in ferrite (>5 µm) are an order of magnitude greater than in austenite. The uniform composition of the low nickel areas is consistent with rapid diffusion in ferrite, whilst the appreciable concentration gradients in the higher nickel regions would be consistent with decreasing nickel solubility in austenite as the $\delta \rightarrow \gamma$ transformation temperature becomes lower, coupled with the lower diffusivity in austenite preventing homogenization during the rapid cooling of the weld. Hence, remnants of solute partitioning from the solidification process could be expected in the as-welded martensitic structure.
Figure 5.10: Calculated weld temperature and diffusion distances in ferrite and austenite as a function of cooling time in a 2.5 mm thick autogenous gas-tungsten arc weld [233].
However, the post-welding tempering treatment at 750°C ought to promote homogenization if the structure was single phase at that temperature. The mean total diffusion distance of nickel in ferrite at 750°C for 6 hours is 1.8 \mu m (D_{Ni} = 1.4 \exp(-245800/RT) \text{ cm}^2 \text{ s}^{-1}) [215]. The discontinuous nickel concentration profile detected in the as-tempered weld material seems to be inconsistent with the premise that the structure is single phase at that temperature. The corresponding diffusion distance for nickel in austenite at 750°C for 6 hours is just 80 \text{ nm} (D_{Ni} = 1.09 \exp(-296800/RT) \text{ cm}^2 \text{ s}^{-1}) [215]. Hence, if instead the structure was two phase at the tempering temperature, with the higher nickel regions preferentially transforming to austenite, the time at temperature would not allow complete solute homogenization across these 1-2 \mu m wide regions - as observed experimentally.

If indeed the structure is two phase at the tempering treatment temperature of 750°C, cooling will result in a fresh martensitic transformation of the austenitic regions. The 'as-tempered' microstructure may then comprise both tempered and untempered martensite.

Whilst not being central to the effects of irradiation on the microstructure of modified FV448 weld metal, the above discussion of the initial microstructure is nonetheless important when discussing the subsequent changes effected by neutron irradiation.

5.2.1.2 Irradiated condition

5.2.1.2.1 Radiation-induced phase change

The most striking microstructural feature of the irradiated off-normal FV448 weld material was the partial transformation of the initially martensitic structure to lath shaped islands of heavily voided austenite. Radiation-induced phase changes in reactor grade steels are not unique. Several instances have been reported of initially austenitic alloys partially transforming to ferrite under irradiation [234-238]. In austenitic alloys nickel is found to segregate strongly to sinks under irradiation and chromium to become depleted. Hence, matrix material remote from point defect sinks is gradually shifted from an initial composition promoting austenite stability to one favouring the formation of ferrite, under the continuing action of radiation-induced segregation.

Instances of the reverse situation, a transformation of an initially ferritic (or martensitic) structure to a partially austenitic structure are rarer. Stubbins [239] examined the phase stability of a series of Fe-15Ni-xCr alloys under ion and electron irradiation. One of his alloys, Fe-15Ni-10Cr, had a two phase microstructure of austenite and martensite on cooling from the austenization temperature. His model alloys were low in impurity content, containing less than 0.005 at.% carbon. The orientation relationship between the
martensite and austenite in the initial microstructure was found to be consistent with that defined by Nishiyama-Wasserman [202,203]. Following both ion and electron irradiation at 450°C reversion within the martensite laths to form precipitates having a face centred cubic structure was observed. The orientation relationship between the two phases was again found to be consistent with the Nishiyama-Wasserman relationship, with several distinct rotations of the fcc phase apparent within a particular bcc region. Stubbins [239] has related the composition of his alloy to the calculated isopleth for Fe-10Cr-xNi alloys [240], revealing that at 450°C his alloy composition lies above the transformation temperature for diffusionless ferrite to austenite conversion. Thus, purely thermal treatment at that temperature would also be expected, thermodynamically, to cause reversion of the martensite to austenite. This was in fact found to be the case. X-ray and magnetic measurements on specimens annealed at 450°C were found to contain less than 5% martensite. The martensitic reversion reaction observed in Stubbins' work may therefore not be radiation-induced, but simply radiation-enhanced.

Another instance of partial transformation of martensite to austenite during irradiation is reported by Hide et al [241]. Their material had the composition Fe-9Cr-8Mo-4Ni, again a model alloy with a low carbon content of 0.0022 wt.%. This material was two phase in the solution annealed condition, consisting of approximately equal volumes of ferrite and martensite. Ageing at 650°C for 100 hours was observed only to cause Laves phase formation in both constituent phases. Ion irradiation at temperatures between 475 and 625°C was found not only to increase the precipitation of Laves phase in the ferrite, but also to cause the formation of heavily voided austenite phase in martensite regions. The austenite began to form at an early stage and grew during the irradiation, to constitute between 30 and 95% of the volume fraction of the martensite phase at the highest damage level of 200 dpa, depending upon irradiation temperature. The volume fraction of austenite phase was greater in the irradiated aged material than the irradiated solution annealed material, with greater swelling also observed in the pre-aged material. This is presumably a result of the decrease in ferrite stabilizing elements in solution caused by the precipitation of Laves phase.

It is interesting to note that austenite did not form in the ferrite phase. The compositions of the ferrite and martensite phases prior to irradiation were not reported, but the martensite would be richer in the austenite stabilizing solute nickel, owing to partitioning at the solution treatment temperature of 1050°C. In terms of overall chromium and nickel equivalents, Hide's alloy [241] is similar in composition to the modified FV448 weld metal of this study: Cr_{eq} = 17.1 and Ni_{eq} = 4.15, compared with Cr_{eq} = 16.5 and Ni_{eq} = 5.1 + 30 x wt.%C. The martensitic phase was found to be stable during thermal treatment at 650°C and thus the formation of austenite was ascribed to the radiation-
induced segregation of nickel to sinks. These nickel enriched regions may then act as nuclei for the transformation to austenite.

An observation of gamma phase (austenite) formation in an initially ferritic Fe-1%Ni alloy has been briefly reported by Takeyama et al [164]. The second phase precipitation was observed to occur at dislocation loops in the electron irradiated alloy, despite the concentration of nickel being well below the solubility limit.

The formation of austenite from an initially martensitic structure during elevated temperature neutron irradiation in this study, when equivalent purely thermal ageing does not cause its formation, may be a radiation-enhanced or a radiation-induced effect. Radiation-enhancement would arise from the increase in diffusivity caused by the excess population of point defects - the radiation-enhanced diffusion described in Section 2.2.2.3. If the equilibrium microstructure at the irradiation temperature for the composition investigated was a two phase mixture of austenite and ferrite then radiation-enhanced diffusion would hasten the attainment of equilibrium.

This possibility has been partly addressed when discussing the microstructure of the as-tempered weld material, where the $Ac_1$ temperature was estimated to be in the region of 755°C. This is clearly well above the actual irradiation temperature of 465°C. Reference to the computer calculated phase diagrams for the ternary Fe-Cr-Ni system at 450°C and 500°C, Figure 5.11 [242], reveals that for austenite to become a stable phase nickel must be present at a concentration of greater than approximately 6%. The regions found to be richest in nickel in the as-tempered weld material, at about 6 wt.%, are hence very close to this boundary. The thermal ageing study of the as-tempered weld material, aged at 465°C for 4656 hours, has shown that the martensitic structure is at least metastable at that temperature. This is also in accordance with transformation temperature curves, $T_o(\alpha\gamma)$, defining the transition temperature from ferrite to austenite in the ternary Fe-Cr-Ni system, calculated by Chuang and Chang [240]. These are marked on isothermal sections of calculated phase diagrams, but are more easily interpreted by means of constructing isopleths for a fixed composition of one component. Such an isopleth for 10 at.%Cr is shown in Figure 5.12. At 465°C a nickel concentration of greater than approximately 11 at.% is necessary to favour the transformation of ferrite to austenite. At a nickel concentration of just 6%, typical of the high-nickel regions in the as-tempered weld material, the transformation requires a temperature of above 680°C to proceed. The evidence thus seems to suggest that for the composition of the as-tempered weld material, reversion of martensite to austenite is neither predicted, nor observed to occur during purely thermal treatment at 465°C. Thus the effect of irradiation would not seem to be simply the hastening towards the attainment of equilibrium from a metastable structure via
Figure 5.11: Isothermal sections of the computer calculated Fe-Cr-Ni ternary phase diagram at (a) 450°C and (b) 500°C [242].

Figure 5.12: Calculated isopleth for Fe-10Cr-xNi alloys, showing the $T_o(\gamma/\alpha)$ transformation temperature [240].
radiation enhancement. Instead, the effect of irradiation appears to fundamentally induce the transformation in some way.

In this study radiation-induced segregation has been demonstrated to occur in FV448 parent plate material under the same irradiation conditions. Chromium was found to become significantly depleted from near to point defect sinks, whilst nickel was observed to become enriched primarily at interstitially biased sinks. Hence at interstitially biased point defect sinks in particular, the local microchemistry alters progressively during irradiation from one promoting the stability of ferrite towards a composition at which austenite becomes the locally stable phase.

The formation of austenite may proceed via either a nucleation and growth type mechanism or a martensitic transformation. The observed morphology appears to suggest that the transformation was martensitic. The austenite phase was present as laths aligned in a common direction within the matrix. Moreover the austenite always had the same crystallographic orientation within a certain region; when more than one orientation relationship between the martensite and austenite was observed, a single austenite zone axis was associated with different bcc zone axes. Although a specific orientation relationship may also occur if a nucleation and growth type mechanism was responsible, more than one growth direction and variant of an orientation relationship would be expected to occur. However, the compositions of the austenite laths differ greatly from the surrounding matrix material; so, clearly, solute redistribution has also occurred. An athermal martensitic transformation occurs without a change of composition, such that the parent and martensite phases have the same composition: it is a diffusionless transformation. In this case, the temperature during irradiation remains (relatively) constant; the parameter varying with time is the local microchemistry. It is this which may provide the stimulus for local isothermal martensitic transformation. Once some austenite is present, the continuing influence of irradiation will promote solute partitioning by the combination of radiation-induced segregation at its interface and radiation-enhanced diffusion increasing the overall diffusivities of the solutes. Thus, once formed, any austenite may undergo compositional modification throughout the course of irradiation.

It is difficult to come to a firm conclusion as to the precise mechanism by which the austenite laths have evolved during the irradiation history, since no time series of specimens is available to characterize the microstructural evolution with increasing damage level (time). Elucidation may be gained by further work to observe the in situ transformation of the modified FV448 weld material during electron irradiation in an HVEM. This would alter the relative balance between operating mechanisms such as
radiation-enhanced diffusion and radiation-induced segregation and may require a
temperature shift to correlate results with this study, but could provide further insight.

Whichever the precise mechanism, both modes of transformation require the presence of
suitable nuclei. Although martensitic transformations are not usually regarded as
nucleation and growth phenomena, in the way that diffusional transformations are, in fact
the nucleation event is the key to a martensitic transformation. Once nucleated, growth
rates reach almost the velocity of sound in the material so that the transformation appears
almost instantaneous. If one of the effects of neutron irradiation on a material was to
facilitate the nucleation of martensitic embryos then the martensitic behaviour of a material
during or subsequent to irradiation would differ significantly from the corresponding
behaviour of unirradiated material. Evidence for such irradiation effects is presented
below, followed by a possible mechanistic explanation for the effects of irradiation on the
generation of suitable nuclei for the bcc to fcc transformation.

5.2.1.2.2 Radiation-affected martensitic reactions

Reports of irradiation affected martensitic reactions are few, and of those many have been
published in the Russian literature. Gruzin et al [243] investigated the effect of electron
irradiation on the martensitic $\gamma \rightarrow \alpha'$ and $\alpha' \rightarrow \gamma$ transformations in iron-nickel alloys.
They reported a marked reduction in the temperature of the reverse $\gamma \rightarrow \alpha'$
transformation, from $400^\circ C$ in the unirradiated alloy to $100^\circ C$ in the alloy irradiated at
$550^\circ C$. The hysteresis of the $\gamma \leftrightarrow \alpha'$ transformation was similarly reduced from $500^\circ C$
to $220^\circ C$. The cause was thought to be the establishment of short range order effects
during irradiation.

Korobeynikov et al [244] determined the effects of proton bombardment on the strain-
induced martensitic transformation in an austenitic steel. In the unirradiated condition a
defformation of 40% was required to induce the $\gamma \rightarrow \alpha'$ martensitic transformation at
room temperature. Proton irradiation caused the strain necessary to induce the
transformation to fall to between just 3 and 4%. This highlights the equivalence of strain-
induced and radiation-induced defects: both promoting the nucleation of martensite.

The influence of neutron irradiation on phase transformations in iron-nickel alloys has
been reported by Bychkov et al [245]. Irradiation was found to cause the starting points
of the direct and reverse martensitic transformations to shift to lower temperatures.

Khan et al [246] studied the effects of bombardment on the formation of martensite in a
plain carbon steel. The ion bombardment was performed at $900^\circ C$ such that the steel was
fully austenitic. The resultant martensite on quenching was found to be finer and harder than the martensite formed in the unirradiated steel. This was attributed to the ion bombardment inducing a higher concentration of lattice defects to form martensite embryos: the increased nucleation density thus producing finer and harder martensite.

Two other studies of irradiation affected martensitic reactions in non-metals have been published. Boron nitride undergoes a martensitic transition from a wurtzite to a graphitic structure: the influence of electron irradiation has been examined by Kurdyumov et al. The wurtzite structure is only metastable, having no region of thermodynamic stability on the phase diagram. The transition to the graphitic structure is achieved by thermal activation at temperatures above 600°C, but its growth rate is relatively temperature insensitive. Electron irradiation was found to stimulate the martensitic conversion to the graphitic form of boron nitride. The superconducting material V_3Si was the subject of neutron irradiation studies by Cox and Tarvin. It was found that irradiation very strongly affects the tendency towards a martensitic transformation, the authors stating that the entropy of the transition is considerably reduced with increasing fluence.

Finally, the effect of low temperature neutron irradiation on the transformation of white to grey tin has been reported by Fleeman and Dienes. White tin, neutron irradiated at -196°C was discovered to transform subsequently to the grey allotrope at temperatures as low as -60°C to -20°C. At such temperatures the unirradiated white tin was completely stable for at least one week. The irradiated tin transformed isothermally at a constant rate with no period of nucleation. The interpretation was that the irradiation treatment artificially introduced a uniform dispersion of nucleation sites for the transformation.

5.2.1.2.3 Martensite to austenite martensitic reversion

Since martensitic transformations are essentially controlled by the nucleation stage alone, any alteration of the transformation by irradiation must be caused by a difference in the population of suitable nucleation sites. The necessity of such sites in the reverse martensitic transformation from a bcc to an fcc structure in iron has been shown by Zerwekh and Wayman. They investigated the reverse transformation in iron whiskers rapidly heated from one end. The transformation occurred with a characteristic accompanying shape change, so that its progress could be followed by observing the passage of the interface with time. The role of suitable nucleation sites was highlighted by the transformation not necessarily nucleating in a region of the whisker nearest the heat source, where the greater degree of superheating would make nucleation in a uniformly heterogeneous structure most likely. The very small volume of the whiskers

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meant that there were few sites at which the transformation could nucleate in a single whisker. The presence of a suitable site proved to be the controlling feature of the transformation, after which the interface moved both backwards against the temperature gradient, and forwards. They detected the habit plane to be close to \{011\}_{bcc} with the orientation relationship predicted to be Kurdjumov-Sachs [201].

Kessler and Pitsch [251] examined the nature of the martensite to austenite reverse transformation in an Fe-33\%Ni alloy. Provided that the heating rate was fast enough, the transition was martensitic with a habit plane close to \{011\}_{bcc} and the relative orientations described by the Nishiyama-Wassermann relationship [202,203]. At very low heating rates the transformation was initially martensitic, but with simultaneous diffusion across the interface as the transformation proceeded. The reduction of nickel concentration in the bcc phase eventually stabilized it against further transformation.

Similar conclusions were reached by Apple and Krauss [252] who investigated the transformation in Fe-Ni-C alloys, where the addition of carbon was found to increase the diffusional component of the mechanism and interfere with the martensitic reaction. Smith and West [253] studied the reversion of martensite in two Fe-Cr-Ni alloys, one essentially carbon-free, the other containing 0.09 wt.\%C. The addition of even this amount of carbon was found to interfere with the reverse transformation: whereas in the carbon-free material complete grains of martensite revert to produce corresponding grains of austenite, in the carbon-containing alloy, each martensite grain produced several regions of reversed austenite misoriented with respect to each other. Finally, in the most recently published work, Abe and Sellars [254] examined aspects of the reverse transformation from martensite to austenite in an Fe-31\%Ni alloy. Despite its very similar composition to the material used by Kessler and Pitsch [251], they instead reported a Kurdjumov-Sachs [201] relationship as defining the relative orientation of the two phases.

5.2.1.2.4 Radiation-induced martensitic reversion: mechanism?

The possible role irradiation plays in nucleating the reverse transformation of martensite to austenite is discussed below. It is proposed that the production of interstitial dislocation loops by irradiation forms sites at which the nucleation of the face centred cubic lattice from the body centred lattice becomes easier, thus lowering the transformation temperature.

The orientation relationships found to exist between the matrix and austenite laths in this work had in common that \{110\}_{bcc} // \{111\}_{fcc}: the closest packed planes in the bcc
structure were very nearly parallel to the closest packed planes in the fcc structure. The {110} interplanar spacing in ferrite is 2.027 Å, compared with 2.070 Å for the {111} interplanar spacing in austenite [199].

A plan view of the usual stacking sequence of {110} layers in a bcc structure is illustrated in Figure 5.13, with equilibrium stacking positions marked a and b. Also marked are two quasi-equilibrium stacking positions lying symmetrically about b, labelled b' and b". These quasi-equilibrium sites lie directly above the triangular interstices of the layer below. The equilibrium sites, b, are at a saddle point between two atoms in the plane below and if the atoms are regarded simply as hard spheres, would in fact be unstable with respect to the sites b' and b". The translation from b to b' corresponds exactly to the effect of an homogeneous shear of \( \frac{1}{3}a[110] \) on a (101) plane from its usual stacking position, b. This shear is accompanied by a contraction perpendicular to the fault plane equal to: \( a\left(\frac{1}{3}\sqrt{2} - \frac{1}{3}\sqrt{3}0\right) = 0.026a \) [255]. This shear is the first step in the Olson and Cohen model [256] for a bcc to fcc lattice transformation and has also been pointed out by Kelly and Groves [257] as a possible shear to nucleate a close packed structure from a normal bcc stacking sequence.

The similarity between atomic positions corresponding to this \( \frac{1}{3}[110] \) fault in a {110} \( bcc \) stacking sequence, caused by this shear from b to b', and the atomic positions for normal stacking in consecutive {111} \( fcc \) planes is shown in Figure 5.14. Of the possible stacking faults on {110} planes in the bcc structure this \( \frac{1}{3}[110] \) fault is estimated to have the lowest energy [258] and therefore to be the most stable.

Interstitial dislocation loops in irradiated ferritic alloys are found to have Burgers vectors of either \( b = \frac{1}{3}a(111) \) or \( b = a(100) \) [191]. Eyre and Bullough [259] proposed that both loop geometries arise from a common loop nucleus consisting of a single platelet of interstitials on a {110} plane. The {110} interplanar spacing is the largest in a bcc structure and the stable configuration for interstitials in a bcc lattice is a split dumbbell oriented in a (110) direction, Section 2.3.1.2.1. Aggregation of single interstitials to reduce their collective strain energy will form a platelet of split interstitials on a {110} plane to nucleate a dislocation loop of Burgers vector \( b = \frac{1}{3}a(110) \). This corresponds to the insertion of an extra plane of atoms in the normal {110} stacking sequence of ababab for a bcc lattice to give a stacking fault of the type abaabab. This stacking fault arrangement will be of extremely high energy since similar atomic layers would be forced into contact. The energy of such an unstable stacking fault configuration will almost certainly be reduced by a lateral offset of the extra plane of atoms. To produce the observed \( a(100) \) and \( \frac{1}{3}a(111) \) type loops, shears of \( \frac{1}{3}a(110) \) or \( \frac{1}{3}a(100) \) respectively.

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Figure 5.13: Plan view of the ideal stacking arrangement of adjacent BCC \{110\} planes, showing both normal and quasi-equilibrium stacking positions.
Figure 5.14: Comparison between plan views of the stacking arrangements of (i) BCC \{110\} planes faulted by $b = \frac{a}{8} [110]$ and (ii) FCC \{111\} planes, normal stacking.
are required to remove the stacking fault. From Figure 5.13 it can be seen that during a shear of \( \frac{1}{2}a[110] \), translating atoms from a to b to remove the stacking fault, the atoms pass directly over the quasi-equilibrium stacking position, b". The contraction perpendicular to the fault plane associated with the stacking position b" may relieve some of the strain energy introduced by the extra plane of atoms lying within the loop and help stabilize the quasi-equilibrium stacking position.

It is this glide on \{110\} planes to the stacking positon shown in Figure 5.14(i) in dislocation loops generated by irradiation which is believed to be the precursor to the formation of an fcc stacking sequence. The slip could conceivably occur either during the transformation of the unstable \( \frac{1}{2}a[110] \) loops to \( a\langle100\rangle \) loops or subsequent to the formation of the latter. Passage of the partial dislocation \( b = \frac{1}{2}a\langle100\rangle \) through an \( a\langle100\rangle \) loop would also correspond to glide to the quasi-equilibrium stacking position. This partial dislocation is stable in the bcc lattice [255,258,260], forming by the dissociation of a perfect \( \frac{1}{2}a[111] \) dislocation according to:

\[
\frac{1}{2}[111] \rightarrow \frac{1}{6}[110] + \frac{1}{6}[112] + \frac{1}{6}[110]
\]

or

\[
\frac{1}{2}[111] \rightarrow \frac{1}{9}[110] + \frac{1}{9}[334]
\]

or by the dissociation of a perfect \( a\langle100\rangle \) dislocation according to:

\[
[100] \rightarrow \frac{1}{3}[110] + \frac{1}{3}[710]
\]

The \( a\langle100\rangle \) type loop has been shown to be strongly biased as a sink towards interstitials, whilst the \( \frac{1}{2}a[111] \) type loop is relatively neutral [191]. Results from Muroga et al [172] implicitly verify this, where nickel was found to segregate to the plane of \( a\langle100\rangle \) dislocation loops in an electron irradiated 12%Cr steel containing 0.9 wt.% nickel, but no tendency for segregation was observed at \( \frac{1}{2}a[111] \) loops. Radiation-induced segregation of nickel to such interstitially biased \( a\langle100\rangle \) dislocation loops in this nickel-modified FV448 weld material would thus be instrumental in stabilizing embryonic fcc \{111\} nuclei formed if such loops were swept by the \( \frac{1}{2}a[110] \) type partial dislocation.

Supporting evidence for the role irradiation-generated dislocation loops may play in the reversion to austenite is provided by the observations of Takeyama et al [164] noted earlier. Their electron irradiated Fe-1%Ni alloy was found to nucleate a nickel-rich phase at dislocation loops (of unreported geometry). The phase was identified by selected area diffraction pattern analysis as gamma phase (austenite).
Suzuki [261] has recently published an overview of nucleation mechanisms of martensite in terms of coordinated slip processes to generate martensitic nuclei within dislocation loops, as shown schematically in Figure 5.15. Results of numerical integration of the equation of motion of a slip plane have shown that starting from almost any displacement pattern around the bcc configuration leads to the displacement pattern corresponding to the fcc or hcp structure for all slips exceeding a certain minimum value.

Such a slip to form an fcc embryo could provide the stimulus for synchronized slips within a particular lath of martensite to revert to the face centred cubic austenitic structure martensitically. The creation of such an embryo is the critical step, since the activation energy for martensitic growth is effectively zero. Once the transformation has been nucleated and the initial interface created, the daughter phase can grow at the expense of the parent, since no new interface is required.

The existence of a single variant of a specific orientation relationship between the austenite laths and matrix within particular regions of the foil, rather than any of the possible 24 variants, implies that the austenite formed on the reversion has the same crystallography as the original austenite: so-called thermoelastic behaviour. This in turn implies that some residual strain energy from the original martensite transformation is present, favouring the particular variants observed. This is reinforced by the observation that where more than a single relationship was found to define the orientation of the austenite laths relative to the matrix within a local area, Figures 4.100 to 4.103, the austenite laths exhibited a single orientation; it was the body centred cubic phase which varied its orientation with respect to the austenite. It was argued above that the 'as-tempered' microstructure of the off-normal weld material prior to irradiation may actually comprise a mixture of tempered martensite and virgin martensite, arising from a two phase structure existing at the tempering treatment temperature. If so, this virgin martensite would have the unrelieved strain energy and carbon supersaturation of the transformation frozen in, providing easier nucleation for the reverse transformation.

The apparent manifestation of more than one defining orientation relationship between fcc and bcc phases in the same material has been previously reported [237,262]. Boothby and Williams' [237] results were consistent with the existence of both the Kurdjumov-Sachs and Nishiyama-Wasserman relationships describing the orientation of irradiation-induced martensite relative to an austenitic matrix in a 12Cr-13Ni steel. Rao [262] found that within a packet of martensite formed within a single austenite grain, both the Kurdjumov-Sachs and Nishiyama-Wasserman relationships were observed to hold, alternating between the martensite laths. The usual relationship reported to hold for Fe-Cr-Ni steels
Figure 5.15: Schematic diagram showing how the synchronized slips of a martensitic transformation (a) can be nucleated at the slip plane of a dislocation loop (b), which is bounded by twin flat coherent interfaces and encircled by an incoherent interface (c) [261].
[263,264] is the Kurdjumov-Sachs. Mazey et al [234] found this to be the case for the irradiation-induced formation of a bcc phase from their austenitic Fe-12Cr-13Ni steel; in contrast, Stubbins [239] showed that the Nishiyama-Wasserman relationship held for the formation of an austenitic phase in a bcc matrix in his ion irradiated Fe-10Cr-15Ni alloy.

However, as stated in Section 4.2.2.1.2 and discussed by various authors [237,262,265,266], it is difficult to determine orientation relationships precisely via selected area diffraction pattern analysis because of errors in zone axis determination. The difficulties may be exacerbated by the use of higher electron accelerating voltages, in this case 300 kV, which flatten the Ewald sphere. The two relationships, Kurdjumov-Sachs and Nishiyama-Wasserman, differ only by a rotation of $5^\circ 16'$ about their common $[110]_{\text{bcc}}$ and $[111]_{\text{fcc}}$ axes. Plan views of the correspondence between the two planes are shown in Figure 5.16. The Nishiyama-Wasserman relationship is symmetrical about the common axes but the close packed directions are misaligned, whereas the close packed directions are coincident in the Kurdjumov-Sachs relationship, but the resulting configuration has lowered the symmetry.

Despite the closeness of the two relationships and the difficulty of accurate zone axis determination, it is felt that the apparent observation of both relationships is in fact representative of the physical situation. Considerable care was taken to maximize the symmetry of the selected area diffraction patterns, thus minimizing the deviations from the zone axes. Moreover, although the orientation of the foil may not be precisely parallel to the desired zone axis, the directions and angles in the plane of the electron diffraction patterns were consistent with the existence of both relationships. A $5^\circ$ rotational misalignment between the diffraction patterns of the two phases would be clear, even if the electron beam was not precisely parallel to the zone axes in question.

5.2.2 Microchemistry

5.2.2.1 Martensite-ferrite interface

The solute concentration profiles determined across the martensite-ferrite interfaces in the irradiated weld material were qualitatively similar to those acquired from boundaries in the irradiated parent plate material. All solutes were found to become locally enriched at the boundary plane, whilst chromium was locally depleted from regions adjacent to the interface. This is not unexpected, since the tempered martensite will have lost its tetragonality and the material both sides of the interface is hence body centred cubic. The discussion of individual solute effects in the parent plate material will thus hold for solute redistribution at interfaces in the bcc weld material.
Figure 5.16: The correspondence between stacking positions and directions in parallel $(111)_{fcc}$ and $(011)_{bcc}$ planes aligned relative to one another as described by (i) the Nishiyama-Wasserman, and (ii) the Kurdjumov-Sachs orientation relationships.
There is a slight difference in the concentration of solutes remote from either side of the interface; this arises from solute partitioning during the welding process. The blocky ferrite is δ-ferrite, formed at high temperature. The adjacent martensite is the transformed product of austenite. Solute partitioning at high temperatures during solidification and cooling of the weld results in the δ-ferrite being slightly richer in the ferrite forming elements chromium and molybdenum than the adjacent martensite.

5.2.2.2 Austenite-ferrite interface

The main feature of solute distribution profiles across the austenite-ferrite interfaces was the extent of solute partitioning between the two phases. Concurrent with solute partitioning are radiation-induced segregation effects to the interface.

Nickel and manganese are both austenite stabilizing solutes; as such they would intuitively be expected, and are observed, to reside preferentially in the austenite phase. Even if, as postulated, the transformation is a martensitic reversion, solute diffusion (enhanced by irradiation) will cause solute redistribution at the irradiation temperature of 465°C. The enrichment of the austenite by nickel and manganese ensures its stability on cooling to room temperature subsequent to irradiation.

Chromium is the classic ferrite stabilizing element, in view of the ferrite-forming tendencies of other solutes being expressed in terms of a chromium equivalent. Thus the preferential incorporation of chromium into the austenitic laths is at first sight surprising. In the binary Fe-Cr system chromium does act to reduce the stability of austenite; similarly in the Fe-Ni system nickel extends the range of austenite stability. In the ternary Fe-Cr-Ni system the composition of phases is not immediately obvious without consulting the phase diagram. Reference to the calculated isothermal sections of the ternary system at 450°C and 500°C in Figure 5.11, reveals that the composition of austenite is actually richer in both chromium and nickel than the ferrite it is in equilibrium with.

The effects of radiation-induced segregation on the composition of the interfacial plane are partly obscured by the greatly differing compositions either side of the boundary plane, compounded by the convolution effects of the finite probe size. In the case of nickel, and to a lesser extent silicon, enrichment at the plane of the interface is observed. This is consistent with the nickel and silicon enrichment detected in the body centred cubic parent plate material, and with strong nickel and silicon segregation to boundaries in irradiated austenitic steels reported in the literature [177,267-271].
Nickel is an undersized solute in an austenitic matrix [272] with a misfit of -3.2%, in contrast to the ferritic matrix [212] in which it has a slightly positive misfit of +4.9%. Nickel is also the slowest diffusing species in Fe-Cr-Ni alloys [273]. Hence the observed enrichment of nickel at interfaces in austenitic matrices under irradiation is in accordance with both mechanisms of radiation-induced segregation detailed previously, Section 2.3. Strong coupling to the interstitial flux in the form of mixed dumbbells and slow relative exchange with the vacancy flux both lead to solute enrichment.

Silicon is significantly undersized in an austenitic matrix, with a misfit of -2.7% [272], and thus its incorporation into mixed interstitial dumbbells and their subsequent migration down the point defect concentration gradient to sinks is the mechanism put forward, explaining its observed enrichment in austenitic materials.

The influence of radiation-induced segregation, if any, on the concentration of chromium and manganese at the interfacial plane is not so apparent - though clearly solute enrichment is not occurring. Relative to the interior of the austenite laths, the detected chromium and manganese concentrations at the plane of the interface are depleted. Relative to the ferrite side of the interface however, the detected boundary plane concentrations of chromium and manganese were enriched. At equilibrium the relative concentrations of each solute in the austenite and ferrite should be uniform to the interface. Hence the X-ray generated solute concentration for, say, chromium should be a measure of the mean of the chromium concentrations in the austenite and ferrite at the interfacial plane, i.e. \( \frac{1}{2}(C_{\text{Cr}}^{\text{a}} + C_{\text{Cr}}^{\text{f}}) \). The width of the transient from \( C_{\text{Cr}}^{\text{a}} \) to \( C_{\text{Cr}}^{\text{f}} \) should be equal to the effective beam diameter and be symmetrical about the plane of the interface. Examination of the detected concentration profiles for chromium and manganese across the interface reveals that the profiles are neither symmetrical about the plane of the interface, nor is the measured boundary concentration the mean of the concentrations in the two phases remote from the plane of the interface and the widths of the transient zones are approximately 20 to 25 nm: far in excess of the beam diameter.

The detected solute concentration profiles for chromium and manganese are therefore not consistent with uniform chromium and manganese concentrations in either phase with a step change at the interface. The observed concentration profiles of these two solutes thus describe real depletion of the solutes from the interfacial region, principally in the austenite. This could be the result of migration of the interface into the ferrite phase at a velocity greater than the diffusivities of chromium and manganese. This seems unlikely in view of the observed concentration profile for nickel, which is a slower diffusing solute than chromium. The alternative, and more likely, cause is depletion of chromium.
and manganese from the boundary plane via radiation-induced segregation. This depletion would be in agreement with previous studies of austenitic steels and the fact that both solutes are oversized \[272\] (Cr misfit = +4.8%, Mn misfit = +3.4%) and faster diffusing species than the host \[215\].

The importance of any segregation to or from the austenite-ferrite interface, however, is less important than the very existence of the interface at all. The actual irradiation inducement of austenite and its resultant void swelling are clearly extremely important microstructural consequences of the radiation damage to this off-normal weld material.

5.2.2.3 Void interfaces

5.2.2.3.1 General

For voids to become stable and grow under irradiation, clearly the vacancy flux arriving at the void surface must exceed the interstitial flux. Since displacement damage creates equal numbers of vacancies and interstitials, there must be an imbalance of point defect fluxes in the system. The generally accepted mechanism is that dislocations develop a stronger interaction with interstitials via their elastic stress fields than with vacancies. The result of this positive bias of dislocations towards interstitials as point defect sinks is that there is an excess of vacancies in the remaining population of migrating defects. Thus, although voids are assumed to be neutral sinks with equal capture efficiencies for vacancies and interstitials, the flux of vacancies to voids is greater than that of interstitials by virtue of their greater concentration in the matrix. Therefore, a precondition for void growth is the presence of interstitially biased sinks in the microstructure: the greater capture rate of vacancies by voids is, in fact, a mirror of the overall bias of other point defect sinks in the microstructure. The greater rate of vacancy absorption means that any vacancy-driven radiation-induced segregation will assume a greater importance at voids, although it is important to realise that interstitially-driven radiation-induced segregation will still operate.

5.2.2.3.2 Voids in austenite

In contrast to solute redistribution profiles at interfaces in the parent plate material where every solute was observed to be enriched at the boundary plane by a combination of thermal and irradiation effects, the mean solute redistribution profiles to the void interfaces in the austenite laths reveal a split between those solutes becoming depleted and those being enriched at the void surface.
The solutes becoming relatively depleted at the void surface were the oversized solutes chromium, manganese, and molybdenum (misfits of +4.8%, +3.4%, +35.9% respectively) [272]. The solutes found to become enriched at void surfaces were nickel, silicon, aluminium and traces of titanium. The first two are undersized solutes in austenite (volume misfits of -3.2% and -2.7% respectively). All four elements are the solutes found to be incorporated in \(\gamma'\) precipitates in irradiated austenitic alloys. The precipitates form as Ni\(_3\)Si in irradiated Type 316 stainless steel [188] and as Ni\(_3\)(Ti,Al) in the nickel based alloy PE16 in the form of a thin shell surrounding the voids [274]. In PE16 the precipitate is formed in the matrix during thermal ageing and is therefore widely distributed. Dark field imaging using one of the \(\gamma'\) reflections is able to reveal the presence of the precipitate as a very thin coating around the void in that instance. However, in this irradiated weld material, \(\gamma'\) was not observed to form as distinct particles under irradiation and thus dark field imaging using a known \(\gamma'\) reflection was not possible to determine the existence of any very thin shell surrounding the voids.

5.2.2.3.3 Voids in ferrite

In contrast to the distinct solute redistribution observed adjacent to the large voids in the austenitic laths, there was an almost complete absence of solute segregation to the much smaller and far less frequent voids detected in the \(\delta\)-ferrite.

One possible explanation is simply that the geometry of the voids and foil is such that any real change in solute concentration adjacent to the void surface is lost amongst the 'background' X-ray signal arising from the matrix through the foil thickness not adjacent to the void itself. The diameter of the voids analysed in the ferrite was typically only 10 nm; however, the foil was also very thin in the regions of the analysed voids, at between 20-30 nm. Thus, although the voids are very small, any solute redistribution fields surrounding them nonetheless occupy a significant proportion of the total foil thickness. Any real substantial solute redistribution adjacent to the voids should therefore be apparent in the X-ray generated solute concentration profiles, albeit less exaggerated than the physical reality.

5.2.2.3.4 Comparison between voids in austenite and ferrite

The difference in observed solute segregation at voids in the two phases may point to fundamental differences in behaviour between void swelling in ferrite and austenite. Clearly, void growth in austenite appears far easier than in ferrite in this material. The radiation-induced austenitic laths will have been exposed to only a portion of the total irradiation period, dependent upon at which point during that period they formed: yet the void swelling within them is visibly orders of magnitude greater than in the ferrite phase.
This is caused by the combination of two factors. Firstly, the incubation period for steady state void growth is often lower in austenitic matrices than in ferritic matrices. Secondly, steady state growth rates of voids in austenite are an order of magnitude greater than in ferrite: swelling rates of approximately 1% dpa^{-1} and less than 0.1% dpa^{-1} respectively. This has been illustrated by the schematic data presented in Figure 1.1.

Void nucleation in commercial austenitic materials can be delayed by careful microstructural control prior to irradiation service. No control at all was exercised in the formation of the austenitic laths in this material, hence it is likely that the incubation dose required for bias-driven void growth will be low, corresponding to the data shown for simple austenitic alloys in Figure 1.1. Moreover, the volume change associated with the body centred cubic to face centred cubic transformation (-1.7%) will encourage the formation of vacancies within the austenite to accommodate the negative misfit. The swelling of the austenite laths, approximately 15%, suggests that the laths have been present for over half the irradiation period. Furthermore, the voids are distributed fairly uniformly across the laths, Figure 4.90, lending further credence to the conjecture that the transformation is a martensitic transformation across a whole lath and not a nucleation and growth mechanism, whereby any voids would tend to be largest in the centre and diminish in size towards the growth interface.

It may seem at first intuitively obvious that the larger voids observed in the austenite ought to exhibit greater solute redistribution adjacent to them. This, however, does not necessarily follow. The growth rate of a void is proportional not to the total point defect flux annealing at its surface, but to the total net difference between the vacancy and interstitial fluxes arriving: it is vacancy-driven growth. High rates of void growth may be achieved either by a large effective bias towards vacancies even for low total point defect fluxes, or by high total point defect fluxes with even just a small effective vacancy bias, or a combination of both. A void may in principle act as a perfect sink to large, almost equally balanced fluxes of vacancies and interstitials, as a consequence exhibit a very low growth rate and yet experience profound solute redistribution adjacent to it. Conversely, if the region surrounding a void shows little solute redistribution, whilst other microstructural sinks do, it implies that the total point defect fluxes to that void are correspondingly low.

The small size of the voids seen in the ferrite could be a consequence of a high incubation dose or a low growth rate, but more probably a combination of both factors. A low void growth rate does not in itself imply a low void sink strength, merely that the net vacancy flux to the voids is correspondingly low. However, coupled with the observation that little solute segregation is apparent at voids in the ferrite when it has been directly detected
at other interfaces and inferred at dislocations from precipitate development, it suggests that the total point defect flux to the voids in ferrite is low. This apparent lack of solute segregation seems to contradict Gelles'\textsuperscript{[6]} assertion that segregation of solutes to voids could be an important factor in the swelling resistance of ferritic/martensitic steels, via an unspecified mechanism. Rather, the low void swelling and absence of segregation seems to point to a more fundamental reason for the low growth rate which results in voids being less efficient sinks in ferrite than austenite during exposure to the same irradiation conditions.

5.3 Overview

5.3.1 Microanalytical considerations

The advantage of the high brightness field emission source in being able to form fine probes with useful currents has been outlined in Section 3.6.1. The smaller lower limit to practical probe size afforded by the field emission source will clearly increase the spatial resolution of analysis, provided that beam broadening by elastic scattering is not too significant. Of at least equal importance is the increase in sensitivity to actually detecting an interfacial segregant. The analytical model developed above, describing the interaction of a Gaussian electron distribution with a slab segregant revealed a clear reduction from true boundary plane concentration to the apparent boundary plane concentration detected by even the field emission source in this work. For a thermionic source the minimum nominal probe diameter to gain useful current, and hence X-ray counts, is 15 to 20 nm. Taking an effective beam diameter of a thermionic source to be 20 nm and the 5.4 nm diameter determined for the field emission source in this work, the necessity of the field emission source for segregant detection is made clear in Figures 5.17 and 5.18.

Figure 5.17 shows the analytically derived concentration profiles for both electron sources modelled for the detection of phosphorus segregation at lath boundaries in FV448 aged at 465°C, compared with the assumed true segregant distribution. The field emission source shows a clear, albeit reduced, peak in concentration at the interface, whilst data obtained from the thermionic source would have to have very good counting statistics to be confident of any peak in concentration. For phosphorus, whether segregation is detected or not is relatively unambiguous; there is effectively 0% phosphorus in the matrix and any significant increase above this detected at the boundary plane shows the existence, at least, of segregation.
Figure 5.17: Effect of beam diameter on theoretical derived concentration profiles modelling phosphorus segregation at lath boundaries in FV448 aged at 465°C, for beam diameters of (i) 5.4nm and (ii) 20nm.
Figure 5.18: Effect of beam diameter on theoretical derived concentration profiles modelling chromium segregation at lath boundaries in FV448 irradiated at 400°C, for beam diameters of (i) 5.4nm and (ii) 20nm.
Take now the situation for chromium at lath boundaries in FV448 irradiated at 400°C. The experimental data was fitted by the analytical model for the field emission source in Figure 5.7. If the effective beam diameter is now 20 nm, as for a thermionic source, the resulting derived concentration profile is as shown in Figure 5.18 with the derived profile for a 5.4 nm beam diameter and the true segregant distribution shown for comparison. Here the gradual depletion towards the interface combined with a boundary plane enrichment would be lost completely in data derived from a thermionic sourced microscope.

It should be clear from the above that the technique of interfacial microchemical analysis via FEGSTEM offers benefits in resolution and sensitivity over conventionally sourced microscopes, whilst it also has distinct advantages over surface analysis techniques in the manner analysis is performed, as discussed previously.

### 5.3.2 Microstructural effects of irradiation

The microstructure of FV448 ferritic/martensitic stainless steel parent plate and off-normal weld material was changed significantly by the gross effects of elevated temperature high dose fast neutron irradiation. Radiation-induced precipitate development, consisting of phases highly enriched in the solutes nickel, silicon and, to a lesser extent, phosphorus, suggested that these solutes undergo significant redistribution under the influence of irradiation. However, once purely thermal effects had been discounted, it was found that the large interfacial enrichments of these solutes implied by the precipitate compositions were not observed. Radiation-induced segregation did not dominate the interfacial microchemistry of the irradiated material. Instead, particularly at the higher irradiation temperature, the interaction of radiation effects with thermal effects is thought to determine the boundary microchemistry.

The cyclic nature of the irradiation may partly explain this. The operation of the PFR, Dounreay, is not uniform: the total effective full power days constituted only between one half and two thirds of the total time spent at temperature in reactor, Table 8. Since radiation-induced segregation is a non-equilibrium event, any time spent at temperature in a reduced or absent neutron flux will result in a partial return towards equilibrium, as the post-irradiation annealing studies showed.

Purely from a scientific viewpoint, the variation of neutron flux and temperature over the period of irradiation coupled with the significant contribution to the gross interfacial microchemistry by purely thermal effects is not ideal for investigating radiation-induced segregation *per se*. Ultimately though, radiation-induced segregation is of technological
interest and, as such, the experimental results from this study are of great interest since
the material has actually been exposed to a real service environment. Thus, the resultant
microstructure is a true reflection of the effects of in-core fast reactor service.

The effect of this in-core service is seen to be not always deleterious. The absence of the
embrittling grain boundary Laves phase reported by other workers [60,61] and confirmed
here is clearly evidenced by the changes in grain boundary chemistry brought about by
the irradiation. Prolonged exposure to temperatures in the range 350-600°C prompts the
unwelcome phenomenon of temper embrittlement in 12%Cr and other alloy steels, caused
by phosphorus segregation principally to prior austenite grain boundaries. In the
irradiated material this segregation was clearly retarded, by a postulated increase in
carbon activity under irradiation.

The behaviour of chromium may be of concern where the resistance of the material to
corrosion is important. Its detected depletion at grain boundaries resulted in
concentrations of approximately 9 wt.% adjacent to boundaries in the irradiated material.
This may leave the components susceptible to localized corrosion, analogous to grain
boundary sensitization in stainless steel weld metal. This may not be so much of a
problem for first-wall applications in fusion reactor designs, but may be more important
for core components in fast breeder reactors which are in contact with liquid sodium.

It is the behaviour of nickel and silicon under irradiation that seem the most critical for the
precise microstructural development in ferritic/martensitic stainless steels. The actual
precipitate phases induced by irradiation seem very sensitive to changes in initial
composition and microstructure. The precipitate phases induced in the FV448 parent
plate material in this study were identified by their chemical compositions and
morphology as M₆X and G phase. Stoter and Little's survey [60] of precipitate
development in a different heat of FV448 under very similar irradiation conditions
reported M₆X, χ phase and, to a lesser extent, σ phase formation, but not G phase. All
these phases contain significant concentrations of both nickel and silicon, but in varying
proportions. The atomic ratio of nickel to silicon typically incorporated in the precipitates
decreases in the order: G phase (2.4:1), M₆X (1.1:1), χ phase (0.44:1) and σ phase
(0.3:1). The atomic fraction that nickel and silicon combined constitute the overall
precipitate composition decreases in the same order: G phase (77%), M₆X (35%), χ
phase (23%) and σ phase (20%).

Although similar in absolute concentrations, the heat of FV448 investigated in this study
varied slightly in relative nickel and silicon concentrations from that quoted in Stoter and
Little's work [60]. The respective concentrations are, for this study, Ni = 0.64%, Si =

321
0.38% (1.7:1); for Stoter and Little, Ni = 0.65%, Si = 0.46% (1.4:1). This seemingly minor change in composition towards a matrix relatively slightly richer in nickel is also reflected in the observed radiation-induced precipitate phases being those also relatively richer in nickel. Similarly, the original observation of G phase precipitation in a neutron irradiated 12%Cr stainless steel by Gelles and Thomas [182] was in HT-9 having respective nickel and silicon concentrations of 0.52% and 0.22% (2.4:1). Thus, despite the substantial solute redistribution necessary for the precipitation of these phases, even small changes in the initial absolute composition seem as though they may influence the radiation-induced phase transformations.

This is further exemplified in the microstructural response of the off-normal FV448 weld material to high dose neutron irradiation. In this instance, the bulk nickel concentration was far in excess of the silicon concentration (4.7% and 0.4% respectively). The resulting phase transformation under irradiation was the formation of austenite. The inducement of austenite from a ferritic/martensitic matrix may have a deleterious effect on the material response to irradiation through loss of structural integrity and dimensional stability caused by void swelling. Significant solute partitioning also occurs leading to, inter alia, the chromium concentration of the ferritic phase to be reduced to between 8 and 9 wt.% with possible consequences for the corrosion resistance of the material. The prevention of austenite formation is not necessarily brought about by simply reducing the nickel concentration of the alloy: Takayama et al [164] observed its formation in a binary iron alloy containing just 1% nickel. Rather, the relative balance between nickel and silicon, as the two solutes found to segregate to point defect sinks under irradiation and as austenite and ferrite stabilizing solutes respectively seems just as critical in determining radiation-induced phase transformations.

Microstructural evolution during irradiation also seems to be sensitive to the role dislocations may play. For given irradiation conditions, the point defect supersaturation is governed by sink strength which is strongly influenced by dislocation density, as was shown in Figure 2.16. At lower dislocation densities the point defect supersaturation is higher and hence the driving force for radiation-induced segregation is correspondingly greater. The FV448 plate in this work was more heavily tempered than the material in Stoter and Little’s study [60]: 6 hours at 750°C compared with 1 hour at 700°C. This heavier tempering treatment leads to a much reduced dislocation density, as reflected by changes in mechanical properties, Figures 2.6 and 2.7. The resultant higher driving force for radiation-induced segregation is evidenced by the formation of G phase in this work, in preference to the phases less highly enriched in the segregating solutes, nickel and silicon.
The significant influence of dislocations is further amplified by the microstructural response of the weld metal to irradiation. Firstly, in the large grains of relatively dislocation-free δ ferrite in the heat affected zone, the only radiation-induced precipitation observed to occur was of G phase, nucleating along dislocation lines. Secondly, the radiation-inducement of austenite in the weld metal at a temperature below which the transformation occurs thermally is thought to be catalysed by radiation generated dislocation loops, which act as easier nucleation sites for the transformation.

Overall, this investigation into the microstructural and microchemical response of FV448 parent plate and weld metal to high dose fast neutron irradiation reveals interplay between irradiation and thermal effects, and a sensitivity to initial microstructure and composition.

5.4 Further Work

The two most unexpected results from this work were: (i) the inhibition of phosphorus segregation to boundary planes during irradiation at temperatures at which it was found to segregate strongly during purely thermal treatment and (ii) the radiation-induced partial transformation of the initially martensitic off-normal weld metal to a duplex austenite/ferrite structure. Mechanisms for both observations have been conjectured, with supporting evidence from the literature where available. However, neither mechanism has been unequivocally proven.

Further work could be directed at determining the effect of carbon activity on the magnitude of phosphorus segregation in alloy steels under irradiation. Model alloys with a fixed concentration of phosphorus could be produced in low carbon and decarburized forms and subsequently irradiated and thermally aged. If the conjecture that irradiation increases the carbon activity which thereby inhibits phosphorus segregation is correct, then the decarburized version of the model alloy should not exhibit the inhibition of phosphorus segregation under irradiation that the low carbon variant will.

The mechanism of the radiation-induced transformation to the duplex austenite/ferrite structure was postulated to be martensitic, nucleating at dislocation loops on {110} planes in the ferrite. Thin foils of the as-tempered off-normal weld metal could be prepared and irradiated in situ in an HVEM to determine how the transformation progresses; whether it is in fact a lath-wise martensitic reversion. Further, the off-normal weld metal has been shown to be at least metastable at the temperature of 465°C in the absence of irradiation. The transformation could be proved to be radiation-induced if the irradiated transformed duplex material were subsequently aged at the irradiation temperature of 465°C, or even a higher temperature that was below the estimated \( \text{Ac}_1 \).
temperature. If the austenite reverted back to ferrite the transformation will have been proven to be radiation-induced. Considerable solute redistribution will be necessary for this to occur and, coupled with the hysteresis effect, a failure to revert to a single phase structure does not invalidate the argument that the transformation is induced by irradiation.

The microchemical and microstructural effects of the irradiation on material properties could also usefully be measured. Service at 465°C is in the classic temper embrittlement range, and usually results in an upward shift in DBTT, a change in fracture mode and loss of upper shelf toughness owing to phosphorus segregation. It would be interesting to determine whether the inhibition of phosphorus segregation by irradiation was reflected beneficially in the impact properties of the irradiated material. The corrosion resistance of the irradiated material could also be evaluated, bearing in mind the chromium depletion observed at boundaries and partitioning within the duplex weld metal structure.

Overall, this study has investigated the microstructural and microchemical response of FV448 parent plate and off-normal weld metal to high dose fast neutron irradiation. Further work determining the macro-properties of the material following irradiation would reveal how these microstructural and microchemical changes affect the bulk properties of the material during in-core service.
CHAPTER SIX
Conclusions

The microstructural and microchemical response of a 12\%CrMoVNb ferritic/martensitic stainless steel, FV448, in the form of parent plate and off-normal weldment, to high dose fast neutron irradiation has been characterized using high resolution microanalytical techniques. Comparisons have been made with thermal control specimens to enable the effects owing purely to irradiation to be determined. The principal conclusions arising from the work are summarized below:

1. The thermal control treatments, ageing at 400 and 465\°C, left the microstructure virtually unchanged from the as-tempered starting condition. In particular, no Laves phase was detected.

2. Thermal ageing at 400 and 465\°C caused solute enrichment at prior austenite grain boundaries and lath boundaries via equilibrium segregation. The magnitudes of enrichment of chromium, molybdenum and phosphorus segregated at boundary planes were directly proportional to one another.

3. Greater segregation was detected at the higher ageing temperature of 465\°C. The relative magnitudes of phosphorus segregation detected at boundaries at the two ageing temperatures were in accordance with McLean's model for the kinetic approach to equilibrium segregation.

4. The absolute magnitude of segregation detected is the averaged concentration in the material volume sampled by the incident electron probe. Analytical modelling of the probe/segregant interaction yielded 'deconvoluted' boundary plane concentrations which approximated the absolute concentrations predicted by McLean's model.

5. Neutron irradiation of the parent plate at temperatures of 400 and 465\°C caused the detected radiation-induced precipitation of M\textsubscript{6}C (\textupsigma) and G phase, both highly enriched in nickel and silicon.

6. The presence of interstitial dislocation loops and very occasional small voids were visible indications of displacement damage. The extremely limited number of voids observed in the parent plate confirms the high resistance to void swelling of the 12\%Cr steels.
7. The net effect of irradiation on interfacial microchemistry in the parent plate material was: (i) to inhibit the (co)segregation of chromium, molybdenum and phosphorus, (ii) to cause chromium depletion from adjacent to boundary planes, (iii) to cause enrichment of silicon at prior austenite and lath boundary planes during irradiation at 400°C and (iv) to cause enrichment of nickel at lath boundary planes only at both irradiation temperatures.

8. The observed directions of segregation of nickel, silicon, chromium and molybdenum were in accordance with previous accelerated simulations and by inference from radiation-induced precipitate compositions. The inhibition of phosphorus segregation was quite unexpected; the reasoning put forward for this observation was that irradiation increases the activity of carbon, which is more surface active than phosphorus and hence displaces it via site competition.

9. In the heat affected zone of the weldment the large grains of δ-ferrite exhibited heterogeneous radiation-induced precipitation only of the silicon- and nickel-rich G phase along dislocation lines.

10. The fully martensitic off-normal weld metal partially transforms to a radiation-induced duplex austenite/ferrite structure during irradiation at 465°C. In contrast, the off-normal weld metal is at least metastable during thermal ageing at 465°C.

11. This radiation-induced formation of austenite in the off-normal weld metal is thought to be a martensitic reversion, caused by radiation generated dislocation loops acting as easier nucleation sites for the transformation.

12. The induced austenite phase exhibited high void swelling, of approximately 15%; the ferrite phase was relatively void-free.

13. The oversized solutes chromium, manganese and molybdenum became depleted from void interfaces in the austenite phase, whilst nickel, silicon, aluminium and traces of titanium were found to become enriched. In contrast, little solute segregation was detected at voids in the ferrite.
14. The technique of EDX via FEGSTEM has several advantages for the detection and measurement of segregation at interfaces, of which perhaps the most fundamental is the ability of the operator to select unambiguously the feature of interest for analysis.

15. Overall, the results within this work and in comparison to previous studies highlight the sensitivity to initial composition, microstructure and heat treatment that 12%Cr steels have in their microstructural response to irradiation.
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