Microstructural control and high-temperature mechanical property of ferritic/martensitic steels for nuclear reactor application

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:


Metadata Record: https://dspace.lboro.ac.uk/2134/32904

Publisher: © G.J. Adetunji

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: https://creativecommons.org/licenses/by-nc-nd/4.0/

Please cite the published version.
<table>
<thead>
<tr>
<th>AUTHOR/FILING TITLE</th>
<th>ADETUNJI, G.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACCESSION/COPY NO.</td>
<td>040013167</td>
</tr>
<tr>
<td>VOL. NO.</td>
<td></td>
</tr>
<tr>
<td>CLASS MARK</td>
<td></td>
</tr>
<tr>
<td>LOAN COPY</td>
<td></td>
</tr>
<tr>
<td>3 Oct 1997</td>
<td></td>
</tr>
<tr>
<td>17 May 2000</td>
<td></td>
</tr>
</tbody>
</table>
MICROSTRUCTURAL CONTROL AND HIGH TEMPERATURE MECHANICAL PROPERTY OF FERRITIC/MARTENSITIC STEELS FOR NUCLEAR REACTOR APPLICATION

By

GBADEGESIN JAMES ADETUNJI BSc, MSc, MRSC, CChem., GradINUEE., MISM

A DOCTORAL THESIS
submitted to Loughborough University of Technology in partial fulfilment of requirements for the award of the degree of doctor of philosophy [PhD].

Supervisors

Dr. R.G. Faulkner, BSc, PhD, FIM
IPTME, Loughborough University of Technology

and

Dr. E.A. Little, BSc, MMet, PhD, MInstP, FIM
Atomic Energy Research Establishment

© G.J. Adetunji.
List of Contents

Certificate of Originality ............................................ i
Dedication ................................................................... ii
Acknowledgements ....................................................... iii
Abstract ..................................................................... iv

1.0.0.0 Introduction .......................................................... 1
1.0.1.0 Materials problem in nuclear power reactors .......... 1
1.0.1.1 Void Swelling .................................................... 2
1.0.1.2 Helium embrittlement of stainless steels ............... 7
1.0.1.3 Blistering ......................................................... 10
1.0.1.4 Sputering ........................................................ 11
1.0.2.0 Demands for nuclear reactor core component materials .................................................. 12
1.0.3.0 Comparison of austenitic and ferritic/martensitic steels ......................................................... 13
1.0.4.0 Aims and Objectives .......................................... 14
1.0.4.1 Historical Background ........................................ 15

2.0.0.0 Literature Review .................................................. 16
2.1.1.0 Heat treatment of 9-12% Cr steel .......................... 17
2.1.1.1 Effect of alloying elements on martensitic reaction ............................................................... 17
2.1.1.2 Tempering of ferritic/martensitic steel .................. 21
2.1.1.3 Temper embrittlement in ferritic/martensitic stainless steel .................................................. 23
2.1.1.4 Ductile fracture in stainless steels ....................... 27
2.2.5.0 Segregation of solute elements ............................... 31
2.3.6.0 Radiation damage in ferritic/martensitic steels .......... 39
2.3.6.1 Calculation of the number of displacements per atom ......................................................... 41
2.3.6.2 Irradiation effect on microstructure in ferritic/martensitic steels ........................................... 45
2.3.6.3 Combined irradiation and high temperature effects .............................................................. 49
2.3.6.5 Radiation-Induced Segregation (RIS) ................... 50
2.3.7.0 Heat loss from a rectangular section plate ............... 55
3.0.0.0 Experimental Work
3.1.1.0 Material
3.1.2.0 Heat treatment 1
3.1.2.1 High temperature fractoographic study
3.1.2.2 Hardness measurement
3.1.2.3 Optical microscopy
3.1.2.4 Surface replica preparation
3.1.2.5 Instrumentation
3.1.2.6 Scanning Electron Microscope (SEM)
3.1.2.7 Dimple size analysis by SEM
3.1.2.8 Transmission Electron Microscope (TEM)
3.1.2.9 Scanning Transmission Electron Microscope STEM)
3.1.3.0 Energy Dispersive X-ray Analysis (EDX)
3.1.3.1 Analysis by STEMMA
3.1.3.2 Preparation of thin foils
3.1.3.3 Preparation of extraction replica
3.1.3.4 Characterisation of secondary carbide particles
3.1.3.5 Quantimet 800 Image Analyser
3.1.3.6 Quantitative and Qualitative Analysis of carbide particles
3.1.3.7 Carbide particle size analysis
3.2.0.0 Modelling of solute segregation
3.2.1.0 Field Emission Gun Scanning Transmission Electron Microscope (FEGSTEM)
3.2.1.1 Experimental determination of solute segregation
3.2.1.2 Analytical Instrument efficiency determination
3.3.0.0 Materials/tensile specimen preparation
3.3.1.0 Heat treatment II
3.3.2.0 Quenching rate determination by experiment
3.3.3.0 High temperature tensile test of unirradiated samples
3.3.3.1 Microstructural analysis
3.3.3.2 Carbide particle analysis
3.3.3.3 Hardness measurement
3.3.4.0 Irradiation procedure
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.4.1</td>
<td>Irradiation dosimetry</td>
<td>85</td>
</tr>
<tr>
<td>3.3.4.2</td>
<td>Calculation of helium generation during irradiation</td>
<td>87</td>
</tr>
<tr>
<td>3.3.4.3</td>
<td>Tensile testing of irradiated specimens</td>
<td>89</td>
</tr>
<tr>
<td>3.3.4.4</td>
<td>Boron autoradiography</td>
<td>89</td>
</tr>
<tr>
<td>3.3.4.5</td>
<td>Thin foil preparation of irradiated specimens</td>
<td>90</td>
</tr>
<tr>
<td>3.3.4.6</td>
<td>Dimple analysis</td>
<td>90</td>
</tr>
<tr>
<td>4.0.0.0</td>
<td>Results</td>
<td>91</td>
</tr>
<tr>
<td>4.1.1.0</td>
<td>Thermally induced microstructure</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>[Heat treatment 1]</td>
<td></td>
</tr>
<tr>
<td>4.1.1.1</td>
<td>Dimple size data [Heat treatment 1]</td>
<td>93</td>
</tr>
<tr>
<td>4.1.1.2</td>
<td>Particle size data [Heat treatment 1]</td>
<td>93</td>
</tr>
<tr>
<td>4.1.2.0</td>
<td>Fracturing at 600°C [Heat treatment 1]</td>
<td>94</td>
</tr>
<tr>
<td>4.2.3.0</td>
<td>Solute segregation models [Heat treatment 1]</td>
<td>95</td>
</tr>
<tr>
<td>4.2.3.1</td>
<td>Experimental data for solute segregation</td>
<td>96</td>
</tr>
<tr>
<td>4.2.3.2</td>
<td>Solute segregation related to mechanical behaviour</td>
<td>98</td>
</tr>
<tr>
<td>4.3.4.0</td>
<td>Quenching rate data</td>
<td>99</td>
</tr>
<tr>
<td>4.3.5.0</td>
<td>Tensile data for irradiated and unirradiated samples</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>[Heat treatment II]</td>
<td></td>
</tr>
<tr>
<td>4.3.5.1</td>
<td>Tensile yield strength</td>
<td>101</td>
</tr>
<tr>
<td>4.3.5.2</td>
<td>Tensile ductility</td>
<td>103</td>
</tr>
<tr>
<td>4.3.6.0</td>
<td>Dimple size distribution for irradiated samples</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>[Heat treatment II]</td>
<td></td>
</tr>
<tr>
<td>4.3.6.1</td>
<td>Ageing for 525 hours at 650°C</td>
<td>107</td>
</tr>
<tr>
<td>5.0.0.0</td>
<td>Discussions</td>
<td>109</td>
</tr>
<tr>
<td>5.1.1.0</td>
<td>Irradiation and thermally induced microstructure</td>
<td>109</td>
</tr>
<tr>
<td>5.1.2.0</td>
<td>Fracture of irradiated and unirradiated specimens</td>
<td>112</td>
</tr>
<tr>
<td>5.1.2.1</td>
<td>Mechanical properties</td>
<td>112</td>
</tr>
<tr>
<td>5.1.2.2</td>
<td>Tensile yield strength</td>
<td>113</td>
</tr>
<tr>
<td>5.1.2.3</td>
<td>Total elongation</td>
<td>114</td>
</tr>
<tr>
<td>5.1.3.0</td>
<td>Fracture related to microstructure</td>
<td>116</td>
</tr>
<tr>
<td>5.1.3.1</td>
<td>Yield strength phenomenon</td>
<td>120</td>
</tr>
<tr>
<td>5.1.3.1a</td>
<td>Crack initiation at particle/matrix interface</td>
<td>122</td>
</tr>
</tbody>
</table>
5.2.4.0  Solute element segregation 130
5.2.4.1  Evidence for solute segregation 130
5.2.4.2  Calculation of detection limit in FEGSTEM 135
5.2.5.0  Solute segregation related to mechanical behaviour 137
5.2.5.1  Embrittlement processes 138
5.2.5.1.1  Fracture before irradiation 138
5.2.5.1.2  Fracture after irradiation 141
5.2.5.1.3  Strain rate dependence of fracture toughness 148
5.3.6.0  Quenching rate data 150
5.3.6.1  Aircooling rate calculation 150
5.3.6.2  Oil quenching (Medium viscosity SAE59) 152
5.3.6.3  Water quenching rate calculation 154

6.0.0.0  Further Work 157

7.0.0.0  Conclusions 159

References 163

Figures 185

Tables 273

Appendix 1 292
Appendix 2 301
Appendix 3 306
Appendix 4 319
Appendix 5 322
DEDICATION

To my wife Moriyike; my children
'Segun, 'Funmi and 'Seun;

My late father, Chief Samuel Aremu Adetunji

and foremost, to the glory of God.
ACKNOWLEDGEMENTS

The author is greatly indebted

(i) To his supervisors, Drs. R.G. Faulkner and E.A. Little; and his director of research, Professor I.A. Menzies; for their guidance and encouragement throughout the period of this study.

(ii) To Dr. J.M. Titchmarsh of A.E.R.E, Harwell and J.S. Bates of IPTME, Loughborough University for operation of FEGSTEM (HB501) and STEM (JEOL-100CX) respectively.

(iii) To D. Stow of A.E.R.E, Harwell for help in the preparation of equipment for tensile testing of irradiated specimens.

(iv) To Centre for Energy Research and Development, University of Ife, Ile-Ife (now Obafemi Awolowo University) for provision of studentship for this project.

(v) To Atomic Energy Research Establishment, Harwell, England, for financial assistance and provision of irradiation facilities.

(vi) To J. Amodio for typing the manuscripts and finally,

(vii) To all whose name are not mentioned but have contributed in one form or another to the successful completion of this course.
ABSTRACT

The materials under study are 9-12% Cr ferritic/martensitic steels, alternative candidate materials for application in core components of nuclear power reactors.

This work involves (1) Investigation of high temperature fracture mechanism during slow tensile and limited creep testing at 600°C (2) Extensive study of solute element segregation, theoretically using proposed model of combined equilibrium and non-equilibrium mechanisms; and experimentally using field emission gun scanning transmission electron microscopy (3) Investigation of effects by thermal ageing and irradiation on microstructural developments in relation to high temperature mechanical behaviour. Quenching rates, tempering temperature and tensile test temperature variations are included in the thermomechanical treatments.

From (1) the results obtained indicate that the important microstructural characteristics controlling the fracture of 9-12% Cr ferritic/martensitic steels at high temperature are (a) solute segregation to inclusion-matrix interfaces (b) Hardness of the martensitic matrix and (c) carbide particle size distribution. These three aspects are all controllable through revised heat treatment procedures and compositional control.

From (2) the results indicate a strong concentration gradients of silicon and molybdenum near lath packet boundaries for certain quenching rates from the austenitizing temperature. The data can be rationalized in terms of non-equilibrium solute segregation processes, which are consistent with estimates of the solute-vacancy binding energy. Possible explanations for the influence of silicon and molybdenum segregation on fracture processes are advanced.
From (3) high temperature tensile data were obtained for irradiated samples with thermally aged ones as controls. The data obtained indicate improvements in tensile yield strength and ductility for certain heat treatments. Explanations advanced include influence of irradiation; solute element segregation and microstructural phase instabilities on mechanical behaviour.
1.000 Introduction

Much nuclear research and development is currently devoted to higher efficiency reactor systems, principally, the fast breeder reactors (FBR), the high temperature gas cooled reactors (HTGR) and the anticipated controlled thermonuclear D-T tokamak fusion reactors (CTR).

A major problem in this venture is the availability or development of materials that can withstand the severe working conditions of these reactor systems. In the CTR systems for example, the first structural wall that faces the plasma directly must be one of very high structural and vacuum integrity. Energy generated in the plasma core passes through the first wall in the form of either high energy neutrons (14 MeV) or as generated heat via interaction of these high energy neutrons and charged particles or neutral atoms with the blanket (Behrisch, 1976). The interaction of these high energy neutrons and charged particles within the first wall material can cause major structural damage. Further damage is possible if impurities in the first wall material undergo transmutation reactions to produce helium or hydrogen gas. Nuclear reactions induced by the neutrons such as (n, p, γ) and (n, α, γ) are sources of an intense γ-radiation (Behrisch 1976). Boron is a known impurity in stainless steel that can undergo (n, α) reactions to produce helium gas. Helium bubbles are known to assist irradiation hardening and cause embrittlement.

1.010 Materials problem in nuclear power reactors

Nuclear power reactor operating experience indicated several problems in core component structural materials. For instance, austenitic stainless steel, when in service,
are greatly susceptible to irradiation-induced void-swelling, in-pile creep and to high temperature helium embrittlement.

1.011 Void Swelling

Basic mechanisms to explain void swelling have been reported in detail by Brailsford and Bullough (1978). During high temperature irradiation (0.3-0.5 $T_m$), void swelling can occur as a direct consequence of the slightly greater drift interaction experienced by interstitials in the stress fields of dislocations compared with the corresponding vacancy interaction. The dislocations thereby act as biased sinks for interstitials, and the result is a potential net excess vacancy flux to any neutral sink available. When nucleation conditions are favourable and in association with gas atoms, eg. helium generated by transmutation or residual gases present in material; the vacancies can aggregate to form void embryos or small gas bubbles. The void embryos are the required neutral sinks and can then grow into voids with the continued net loss of interstitials to the biased sinks. The two essential requirements for void growth to occur (in the appropriate temperature range) are (i) the presence of biased sinks (dislocations) and (ii) the presence of neutral sinks (three dimensional void embryos stabilised by gas atoms). However, the magnitude of the dislocation bias for preferred interstitial capture is fundamental in governing the rates of void and dislocation loop growth (E.A. Little 1980). The detailed mechanism in which void nucleation and growth takes place is critically dependent on the nature and behaviour of the surrounding initial dislocation network and the subsequent development of the irradiation-induced dislocation substructure.
If the initial dislocation density is not too large, then the interstitials, as the more mobile point defects, rapidly aggregate to form interstitial dislocation loops, during the early stage of irradiation. These dislocations then provide the biased sinks for point defects. The enhanced flow of interstitials into these loops then causes their growth, coalescence and ultimate incorporation into the dislocation network.

But for material with a very high initial dislocation density, the nucleation of both interstitial dislocation loops and voids is inhibited as a result of the dominance of point defect recombination at the dislocation sinks. The onset of void swelling is thereby postponed.

In the case of helium gas assisted void swelling at elevated temperature, nucleated bubbles are usually not in equilibrium state until compressive stress developed by a cluster of helium atoms is overcome. High density of vacancies provided via irradiation can eliminate the strain field formed and bubbles can attain equilibrium. If the pressure inside the bubble of radius \( r \) is \( P \) and surface energy is \( \gamma \) we can write

\[
P = \frac{2\gamma}{r} \quad (1.011)
\]

If \( N \) is the number of gas bubbles formed per unit volume of the alloy, and \( n \) is the number of gas atoms in each bubble; the perfect gas law can be assumed and we can write

\[
P \frac{4\pi r^3}{3} = nkT \quad (1.012)
\]

If bubbles are of equal sizes, the fractional swelling due to these gas bubbles can be written as
In practice, bubbles have been observed to have different radii and by a distribution function, \( N(r)dr \), we can describe the density of bubbles.

\( N(r)dr \) indicate the number of bubbles per unit total volume with radii ranging from \( r \) to \( r+dr \). The total bubble density, then, can be given as

\[
N = \int_{0}^{\infty} N(r)dr \tag{1.014}
\]

and the volume swelling due to helium gas bubbles can be estimated from

\[
\frac{\Delta V}{V} = \frac{4\pi}{3} \int_{0}^{\infty} r^3 N(r)dr \tag{1.015}
\]

Furthermore, from equation 1.012, we can obtain \( r \), the average bubble radius as

\[
r = \frac{\sqrt[3]{3nkI}}{8\pi\gamma N} \tag{1.016}
\]

and the fraction swelling as

\[
\frac{\Delta V}{V} = \frac{4\pi r^3 N}{3} = \left( \frac{nkI}{2\gamma} \right)^{3/2} \left( \frac{3}{4N} \right)^{1/2} \tag{1.017}
\]

If bubbles are small, and the pressure in each bubble is large, the ideal gas law is no longer valid and then, the Van der Waal's relation can be employed to obtain swelling fraction as
If there is a uniform interbubble spacing, \( d \), then, each bubble of volume \( \frac{4\pi r^3}{3} \) is contained in a volume of approximately \( d^3 \) and hence

\[
\frac{\Delta V}{V} = \frac{\frac{4\pi r^3}{3}}{d^3}
\]

(1.019)

By eliminating \( r \), we have

\[
\frac{\Delta V}{V} = \left(\frac{3}{4\pi}\right) \left(\frac{\text{Ind}/546\gamma}{d^3}\right)
\]

(1.020)

This deduction is an important parameter technologically. If a material under irradiation at elevated temperature can be obtained in which helium bubbles remain finely dispersed, their sizes will always be small, pressure in them will be high and very little volume swelling will be produced. [Greenwood, G.W. et al 1959, Barnes and Nelson, 1965].

Anderko (1980) investigated void swelling in 12% Cr ferritic/martensitic steels. Peak swellings were observed for charged particles irradiation of HT9 at 500°C and for neutron irradiation of 1.4914 at ~ 400-500°C.

Harris (1983), in his review, presented considerable evidence for void swelling after, electron, charged particles and neutron irradiations of ferritic/martensitic steels.

Little (1979) proposed a likely mechanism for the low void swelling of the ferritic/martensitic steels. Explanations include (i) the trapping of irradiation-induced vacancies
by the interstitial solutes, carbon and nitrogen, and substitutional solutes, thereby enhancing mutual point defect recombination (Hayns and Williams, 1978) (iii) strong interactions of the dislocations with interstitial solutes or mixed interstitial and substitutional solute atmospheres leading to a reduced dislocation bias for preferential self-interstitial capture and/or inhibition of the climb rate of the dislocations. (iii) formation of the interstitial dislocation loops with a \langle 100 \rangle Burgers vector within a network of predominantly $\frac{a}{2} <111>$ dislocation loops. (iv) suggestions that the relaxation volume of self interstitials is significantly lower in the bcc steels than in the fcc austenitic steels, hence reducing the bias for preferential absorption of interstitials at dislocations, and a subsequent decrease in rate of void nucleation and growth.

The loops with \langle 100 \rangle Burgers vector constitute biased sinks for interstitial point defect capture whilst those with $\frac{a}{2} <111>$ are relatively neutral sinks. The vacancy super-saturation induced by preferential growth of a \langle 100 \rangle dislocation loops by interstitial capture are absorbed by the relatively neutral $\frac{a}{2} <111>$ sinks to suppress void nucleation.

The void swellings for the fast reactor irradiated 10-12\% Cr ferritic/martensitic steels; (Gelles 1981; Little 1979, Scherbak et al, 1977, Huet et al, 1979, Powell et al, 1981, de Bremaecker et al, 1983), are generally considerably lower than those determined following electron and ion irradiations to comparable doses.
1.012 Helium Embrittlement of Stainless Steels

Austenitic steels, high integrity cladding materials in fast breeder reactors are found to embrittle severely at high temperatures above 600°C. This has been attributed to the action of helium generated by the principal constituents of the steels and impurities such as boron. [Braski, 1979]

The current accepted explanation for helium embrittlement is that bubbles of this gas act in some manner on the grain boundaries, which are structurally weakened and thus end up in causing a premature intergranular fracture and a loss of ductility. [Matsumoto, K. et al, 1977] The loss of ductility is likely to be associated with the displacement of helium bubbles toward grain boundaries during high temperature straining; which would imply the existence of a correlation between fracture behaviour and the rate of strain applied under these conditions. [Lane and Goodhew, 1984]

Previous reports on the embrittlement of austenitic steels irradiated with α-particles revealed that the ductility at high temperature decreases with the increase of either testing temperature or helium dosage or both and that this ductility loss is not enhanced by post-irradiation annealing for 10 hours at 750°C. Also, that ductility is enhanced with increasing strain rate. This indicates that helium embrittlement is likely to be governed by a thermal activation process and that the collection of helium atoms along grain boundaries, causing intergranular fracture proceeds at a finite pace, the collection remains uncompleted when the rate of straining is very rapid.

Keishi Matsumoto et al (1977) explained that rapid straining leaves bubbles strung along the grain boundaries,
but that on close observation, they are not precisely aligned on the boundary as it was the case with slow straining; and the bubbles on or near the boundaries are distinctly smaller both in size and number than with slow straining, despite the greater stress and strain applied. These workers then considered two mechanisms to explain the gathering of helium bubbles along grain boundaries during straining: (1) moving dislocations sweeping the bubbles toward the grain boundaries [Barnes, 1965] and (2) grain boundary collection of bubbles during migration.

It can therefore be concluded that the premature intergranular mode of failure is caused by the trapping of small helium bubbles in the grain boundaries and that the agglomeration of these small bubbles into large bubbles at grain boundaries can act as voids which can grow into cracks through the action of grain boundary sliding.

In contrast, the 9-12% Cr ferritic/martensitic steels such as the one under study exhibit no helium embrittlement under high temperature irradiation. Wassilew et al, (1983) reported small helium bubbles present on martensitic lath, lath packet and prior austenite boundaries with no significant reduction in ductility. This observation was explained by Wassilew that the strong embrittlement of austenite steels was enhanced by the special role of twin planes as the most efficient area of increased vacancy production and takes into account their ability to transport these vacancies with reduced energy and low loss into high angle grain boundaries. Since martensitic steels do not possess twin boundaries one could argue that the main vacancy source for the growth of the small helium bubbles is lost. Contrary views advanced by Faulkner and Anderko (1983) was that martensitic steels have higher inherent
resistance to intergranular fracture even for unirradiated materials. This is caused by a high stacking fault energy, a higher difference between surface and grain boundaries energies and a finer "effective" grain size as opposed to austenitic alloys. Several other workers [Little et al, 1982, Gelles et al, 1983; Ulrich Stamm and H. Schroeder, 1987] have confirmed ferritic steel resistance to helium embrittlement during elevated temperature irradiations.

Klueh and Vitek (1983), from their tensile tests on 9Cr-1MoNb and 12Cr-1MoVW steels; observed no detrimental effects of irradiation or helium concentration. There was no indication of decrease in ductility due to irradiation. Their material containing 2% Ni produced the largest amount of helium and had the highest ductility (>20%). They concluded that ferritic/martensitic steels are quite resistant to elevated temperature helium embrittlement.

Luklinska (1985) reported that helium bubbles nucleate homogeneously in the matrix of ferritic steel, but the growth is slow at all temperatures up to 850°C. Stamm and Schroeder (1987) concluded that the implantation of helium at high temperatures shows no drastic effects on the mechanical properties of martensitic steel (DIN 1.4914). No helium embrittlement occurred even at helium concentration up to 3000 appm (873K) and 2700 appm (973K). Specimens with highest helium content at 973K show small portions of intergranular rupture.

Bullough and Jenkins (1987) studied four irradiated 20% Cr 25%Ni austenitic alloys with additions of Nb, Ti and B. Post-irradiation creep tests indicated that the highest helium levels did not coincide with the greatest embrittlement. Helium bubbles were found too small to nucleate creep cavities directly.
Baker et al (1987) observed microscopic helium bubble population in AGR fuel cladding material (20/25/Nb) after post-irradiation stress-rupture testing.

1.013 Blistering
For a non-soluble incident gas ion in a metallic alloy, transmission electron microscope observations have shown that, at bombarding doses of $>10^{20}$ ions/m$^2$ corresponding to 5-10 atomic percent gas injected into solid, the gas starts to coalesce to small bubbles of 1 to 3nm diameter inside the implanted layer [Roth, 1975]. If the ion bombardment dose is increased further, blisters (bending up of a surface layer) can be observed. The critical doses for the appearance of blisters lie between $10^{21}$ to $10^{22}$ ions/m$^2$. These doses depend on the bombarding energy, the current density, angular and energy spread of the bombardment as well as the material and its temperature [Erents, 1973].

Blistering and its mechanism have been variously investigated within the last few years because it had been assessed as the most dangerous source for fusion reactor first wall erosion problems. It was found that the bending up of the surface layers is basically caused by the release of lateral stress produced in the implanted surface layer. At medium temperatures ($500^\circ$ to $800^\circ$C) blistering generally is increased and large exfoliation of the blister covers can be observed. On increasing temperature further, blistering is decreased and an equilibrium surface structure can be observed at lower bombarding doses. For a fusion reactor operating, blistering may possibly contribute to first wall erosion at the start of operation. The angular and energy distribution of the ions bombarding the first wall may
prevent blistering from the start due to increased wall temperature. An equilibrium structure at the surface may form already after the first few discharges. Sputtering yields generally have been obtained with doses well above the dose for blisters and thus include blistering. The sponge-like structure found after high dose ion bombardment will have different mechanical, thermal and electrical properties compared to the unbombarded material. [Furth, 1972]

1.014 Sputtering
Physical sputtering is the removal of surface atoms from a solid via a collision cascade initiated in the near surface region by incident energetic particles like ions, neutrons or electrons. Sputtering can be considered as radiation damage on the surface. During the spread of the cascade, the surface stays cold contrary to surface erosion by evaporation. The sputtering yields (atoms per incident particles) are proportional to the energy deposited by the incident particles in the surface layer in nuclear motion and inversely proportional to the surface binding energy. [Sigmund, 1969].
1.020 Demands for nuclear reactor core component materials

The choice of a design criterion for the fusion and fission reactors core structural components (first wall, cladding/wrappers) will depend on appropriate material selection to give properties that will ensure a significant service life. (Adetunji, 1985). Selected materials would need to exhibit the following properties:

i) Low activation

ii) Low hydrogen or helium gas production

iii) Low neutron radiation damage effect in the temperature range of application

   ie. low void swelling, low helium embrittlement and minimum loss of ductility.

iv) Low irradiation creep

Since the fast breeder and controlled thermonuclear fusion reactors will probably operate at high temperature, in order to obtain good thermal efficiency, core or near core materials/structures should further possess

a) Good elevated temperature mechanical strength, endurance limit of up to 700°C

b) High vacuum integrity at elevated temperature

c) Good resistance to thermal fatigue to withstand cyclic thermal loading in pulsed reactors

d) Good welding and fabrication characteristics

e) Good corrosion resistance

Clearly, it may be difficult to obtain a material capable of fulfilling all these requirements. Nevertheless, recent high temperature materials research and development has indicated likely materials such as (i) stainless steels and nickel base alloys (ii) carbides eg. silicon carbides and (iii) refractory metals and alloys eg. Nb-1%Zr, Mo, V.

[D. Harries, 1983]
Comparison of austenitic and ferritic/martensitic steels

Austenitic stainless steel (M316) in the cold worked condition is a known candidate material in FBR cladding and subassembly wrapper applications. For a design peak burn up of 10% for the fuel pins in PFR (Prototype Fast Reactor), the corresponding maximum displacement dose in the austenitic alloy cladding and wrapper is approximately 76 dpa (NRT), the gas production is typically <100appm He and <1000appm Hydrogen depending on alloy composition.

The displaced atoms and/or helium generation produce radiation hardening and embrittlement; void swelling and irradiation creep in austenitic steels [D. Harries, 1977, 1978, 1979, 1982].

The 9-12%Cr Ferritic/martensitic steel is an alternative to austenitic steel as a candidate for applications in subassembly wrapper components. It is also nominated for application in the CTR first wall. As against the austenitic steel, the 9-12% Cr martensitic steel shows high void swelling resistance to displacement doses in excess of 100 dpa in reactor variations, lower degree of post-irradiation embrittlement, lower thermal expansion coefficients and high compatibility with sodium.

However, 9-12% Cr martensitic steels have their DBTT increased under irradiation and their upper shelf energy decreased. Hydrogen embrittlement is also worse in this material [E.A. Little, 1987].
Aims and Objectives

Based on material problems discussed in earlier sections, one of the design criteria that require review very closely is the ductile-brittle transition temperature for ferritic/martensitic steels. It is valuable to understand the high temperature failure mechanism for two reasons.

(i) The distinction between post-irradiation embrittlement mechanisms in ferritic and austenitic steels can be made clearly on a microstructural basis.

(ii) Factors governing the fracture can be understood so that the onset of brittle fracture (DBTT) may be moved to lower temperatures by microstructural modification.

These two demands when achieved for ferritic/martensitic steels will assist in the further development of these alloys by suitable treatment and composition control. Non-equilibrium solute segregation may also influence embrittlement and fracture behaviour. This phenomenon has not previously been investigated in the martensitic stainless steels. It is considered appropriate to include investigation of solute segregation in the overall research programme in order to identify the interacting solute species.

Furthermore, it is expected that the material will be applied in the core areas of nuclear reactors - fission and fusion. Investigation of irradiation effects on high temperature mechanical behaviour of 1.4914 steel is essential.
Hence, the research programme was set up in order to obtain relevant outcomes to explain the following effects on high temperature microstructural development and mechanical behaviour of ferritic/martensitic steels.

(a) Effect of dimple size distribution
(b) Effect of stress (Creep and Tensile Test)
(c) Effect of Nb stabilisation on 1.4914 steel
(d) Effect of tempering temperature
(e) Effect of ageing and creep treatment time
(f) Effect of cooling rate
(g) Effect of heat treatment variables on carbide particle distribution and lath size
(h) Effect of prior austenite grain size and hardness and ductility
(i) Effect of solute segregation as a function of cooling rate and solution treatment temperature
(j) Effect of irradiation.

1.041 Historical background
Part of this work has been undertaken at Loughborough by R.G. Faulkner, W.E. Voice, P. Maheswaran and J.S. Bates.

Their contributions are reflected in sections 3.1.2.0; 3.1.2.4; 3.1.2.1; 3.1.3.1; 3.1.2.2 and 3.1.2.3 described in the experimental chapter of this thesis.
2.0.0.0 Literature Review

2.1.1.0 Heat treatment of 9-12% Cr Steels

In the present study, various heat treatments were applied on ferritic/martensitic steel in order to obtain a fully martensitic microstructure. Since it is included in the aims of this project to relate high temperature mechanical behaviour to microstructural evolution, it is useful to highlight the effects of austenitizing and tempering heat treatments on the microstructure and mechanical properties of 9-12% Cr steel. However, no attempt is made in this section to review the γ/α transformation since, this is available in the literature [Honeycombe (1981) and Christian (1970)].

The amount of martensitic phase formed during transformation depends on (i) Solution treatment or austenitizing temperature (ii) Composition of the steel and (iii) cooling rate from austenitizing temperature.

Alloying elements such as C, N, Ni, Mn and Co are known to stabilise the austenite phase while Cr, Si, Mo, W, V, Al, Ti and Nb will stabilise the ferrite phase [Fig. A.0.0, A.0.5, and A.0.2]. The strength of the steel before tempering is related to the proportions of δ-ferrite and martensite obtained after transformation. Hence, it is important to know the relative amounts of δ-ferrite and martensite formed after cooling from higher temperature. [Little 1977].
TheMs and Mf denoting temperatures at which martensite formation start and finish respectively, are linearly related to the steel composition. The alloying additions of Mo, V, and Nb are to increase tempering resistance and refinement of prior austenite grain size. The TTT curve is very useful in explaining the α/γ transformation. [Fig. A.0.0 and A.0.4].

The faster the cooling rate, the more purely martensite formed [Schirra 1984]. The nose of curve between ACle and Ac1b indicate paid formation of the carbides while that below Ac1b temperature indicate rapid formation of the pearlite at austenitizing temperature of ~1080°C. The effect of silicon, molybdenum and niobium on the reaction rate inhibit the formation of the pearlite by pushing the curve nose to longer transformation times. Figures A.0.4 and A.0.5 show the effect of carbon content on the type of martensite and the amount of retained austenite in Fe-C alloys.

2.1.1.1 Effect of Alloying elements on martensite reaction
Interstitial solutes such as carbon and nitrogen have much larger effect than the metallic ones. Relative effect of other alloying elements can be shown, according to Andrews, (1952) as

\[ M_g (°C) = 539 - 423 (%C) - 30.4(%Mn) - 17.7(%Ni) - 12.1(%Cr) - 7.5(%Mo) \] 2.1.1.50

Zener (1946) in his thermodynamic analysis using a binary Fe-X system, explained the effect of alloying elements on the austenite/martensite transformation. If chemical free energy of the austenite phase is \( G^\gamma \) and that of martensite phase is \( G^\alpha \); in the austenite
\[ G^\gamma = (1-x)G_{Fe}^\gamma + xG_x^\gamma + G_M^\gamma \]  

where \( x \) = atomic fraction of alloying element:

- \( G_{Fe}^\gamma \) = Free energy of Iron in the \( \gamma \)-form
- \( G_x^\gamma \) = Free energy of X in the \( \gamma \)-form
- \( G_M^\gamma \) = Free energy of mixing of austenite

Similarly,

\[ G_\alpha^\gamma = (1-x)G_{Fe}^\alpha + xG_x^\alpha + G_M^\alpha \]  

\[ G^\gamma - G_\alpha^\gamma = \Delta G_{Fe}^{\alpha \gamma} = (1-x)G_{Fe}^{\alpha \gamma} + xG_x^{\alpha \gamma} + \Delta G_M^{\alpha \gamma} \]

Zener assumed that the solid solutions were sufficiently dilute to be ideal, and the mixing term \( \Delta G_M^{\alpha \gamma} \) becomes zero. So we have

\[ \Delta G_x^{\alpha \gamma} = \Delta H_x^{\alpha \gamma} - T\Delta S_x^{\alpha \gamma} \]

where \( \Delta S \) = entropy change between \( \alpha \) and \( \gamma \)

\( \Delta H \) = enthalpy change and \( T \) = temperature.

Furthermore,

\[ \Delta G_x^{\alpha \gamma} = RT \ln \frac{X_\alpha}{X_\gamma} \]

Where \( X_\alpha \) and \( X_\gamma \) are the compositions of \( \alpha \) and \( \gamma \) in equilibrium with \( \gamma \) and \( \alpha \) at any temperature.

By assuming that \( RT \ln \frac{X_\alpha}{X_\gamma} \) is constant and that \( \Delta S_x^{\alpha \gamma} \) is zero; for ideal solutions
\[ \Delta H_{x}^{\alpha \rightarrow \gamma} = R T \ln \frac{x_{\alpha}}{x_{\gamma}} = \Delta H_{x}^{\alpha \rightarrow \gamma} \]  

2.1.1.56

This equation can be described as the difference in enthalpies of alloying elements \( X \) in the austenitic and martensitic phases.

Rewriting eq. 2.1.1.53

\[ \Delta G_{x}^{\alpha \rightarrow \gamma} = (1-x) \Delta G_{Fe}^{\alpha \rightarrow \gamma} + x \Delta H_{x}^{\alpha \rightarrow \gamma} \]  

2.1.1.57

When \( \Delta H_{x}^{\alpha \rightarrow \gamma} \) is obtained; \( \Delta G_{x}^{\alpha \rightarrow \gamma} \) can be evaluated. Values for \( T_{o} \), the temperature at which \( \gamma \) and \( \alpha \) have the same free energies can be evaluated by putting \( \Delta G_{x}^{\alpha \rightarrow \gamma} \) equal to zero.

Since alloying elements either expand the \( \gamma \)-loop ie. stabilize \( \gamma \) or contract the loop and promote \( \alpha \)-formation, there would be different effects of alloying elements on \( \Delta H_{x}^{\alpha \rightarrow \gamma} \). Elements which expand the \( \gamma \)-loop will make \( \Delta H_{x}^{\alpha \rightarrow \gamma} \) to be negative, and lower \( T_{o} \) whereas elements which favour \( \alpha \)-formation will make \( \Delta H_{x}^{\alpha \rightarrow \gamma} \) positive and raise \( T_{o} \) [Fig. A.0.1].

\( \Delta H_{x}^{\alpha \rightarrow \gamma} \) values of alloying elements are available in the literature.

Cohen and coworkers (1962) have provided detailed data for iron-carbon alloys between 0 and 1.1 wt% carbon. It was found that the driving force \( \Delta G_{x}^{\alpha \rightarrow \gamma} \) at the \( M_{s} \) temperatures of the alloys was practically constant, and approximately 1250 J mol\(^{-1}\) independent of carbon content.[Fig. A.0.6 & A.0.10].

However, work on iron-nickel alloys showed that the driving force increases with increasing nickel content ie. as the \( M_{s} \) is depressed.
It is important to note that chromium, though contracts the \( \gamma \)-loop can still have a negative \( \Delta H \) value, if \( \Delta H \) is obtained at a very low temperature. Silicon is an \( \alpha \)-stabiliser and will expand the \( \alpha \)-loop. Molybdenum addition will inhibit the formation of the pearlite by pushing the transformation curve to longer times. The presence of silicon and molybdenum influence large formation of pure martensite structure. [Figs. A.0.0, A.0.2 and A.0.8].

Substitutional solutes (Mn, Ni, etc) do not greatly influence the strength of the as quenched martensite. The role of these solutes is chiefly to slow down the tempering reactions. Silicon is known to stabilise \( \epsilon \)-iron carbide so that it may persist up to higher tempering temperature. (Nutting, 1983).

\( \text{Cr}, \text{Mo}, \text{V}, \text{Nb} \) are carbide forming elements. They are \( \alpha \)-stabilizers. They tend to decrease the composition range over which \( \gamma \)-phase is stable and also to raise the temperature at which a fully austenitic structure can be obtained. They greatly increase the hardenability of the steel making it possible to obtain martensite structures even at slower cooling rates. [Figs. A.0.0, A.0.3 and A.0.8].

The addition of small amounts of interstitial elements (C, N, O) and usually large amounts of substitutional elements (Mn, V, Ni) can alter the DBTT of ferritic steels. Direct effects of solutes include solid solution, strengthening or changing of deformation mode (twinning, cross ship etc affecting \( k_y \)) and hence; the friction stress and the yield stress. [Wullaert, 1970].

According to Mott and Nabarro (1948) the athermal component of the friction stress (Petch equation should be linearly proportional to alloying element concentration.
Fleisher (1963) attributed solid solution hardening to difference in the atomic size and modulus of the solvent and solute elements.

Rees et al (1954) and Stoloff et al (1965) reported that silicon, vanadium and cobalt as alloying elements can raise the DBTT of ferritic steel. Manganese lowers the DBTT and raises the impact shelf energy of ferrite with fracture toughness improving as Mn-carbon ratio increases [Barr et al (1947), Allen et al (1953)]. [Fig. A.0.2] The beneficial effects of Mn on fracture behaviour of ferrite, are attributed to the prevention of carbide films at grain boundaries and the lowering of Ky [Stoloff et al 1965]].

2.1.1.2 Tempering of ferritic/martensitic steel

Tempering response of ferritic/martensitic steel depends largely on the carbon content of the original austenite (Nutting, 1983). When the carbon content of the starting austenite does not exceed 0.2%, the martensite produced forms at high temperature and consists of bundles of laths or pencils with each sub unit having a high and uniform dislocation density. The supersaturated bct solid solution which is metastable at lower temperature decomposes into aggregates of ferrite and carbide at a higher temperature range. Tempering caused microstructural changes by (ι) relief of internal stresses associated with the lattice shear (ιι) restoration of ductility and toughness, though at the expense of strength and hardness. [Schirra (1984), Materna Morris et al (1987)]. In general, high strengths can be achieved on tempering at lower temperatures when acicular nature of the martensite is essentially retained.
As tempering temperature increases, tempered strength decreases since carbon will move out of the supersaturated solid solution and cause change in crystal structure from bct to bcc. At higher temperature, say 750°C, tempering can cause successive changes in microstructural parameters such as lath size, carbide size and distribution. [Fig. A.0.7] [Nutting, 1983]. As tempering temperature increases, the grain size increases but the growth of grains is governed by Oswald ripening of the carbides. The formation of carbides during tempering can influence the rate of carbon removal from supersaturated solid solution in the matrix.

Though, carbides provide barriers to dislocation motion to encourage hardening as predicted by Ashby-Orowan expression; for low carbon steels this is not the case since carbides hinder to dislocation motion cannot arrest the decrease in hardness due to the loss of the interstitial solute. Hence, softening becomes predominant.

According to Nutting (1983), the Ashby-Orowan expression cannot hold when tempering above 450°C. At higher tempering temperature, the flow stress can no longer be dependent upon the dispersion of carbides but upon the ferrite grain size. The precipitation of carbides from the martensite can cause an increase in the activation energy of the softening processes to levels comparable to the activation energy for self diffusion in iron.

Little et al (1977) observed precipitation of alloy carbides of the $M_2X/Cr_7C_3$ type within the martensite laths after tempering above 500°C. Rapid averaging of $M_{23}C_6$ also occurred at the martensite lath boundaries. Tempering at 650°C is associated with growth of $M_{23}C_6$ carbides at lath boundaries and a further decrease in dislocation density. The dislocations began to line up as sub-boundaries across the laths and the $M_2X$ precipitates in the $\delta$-ferrite region.
begin to grow as needles. The 750°C tempering can cause the growth of subcells within the martensite laths into fairly equiaxed subgrains, large M$_{23}$C$_6$ precipitates, coarsening of M$_2X$ needles in the δ-ferrite and removal of matrix M$_2X$ from within the martensite laths. Polygonised networks or sub-boundaries with further coarsening of M$_{23}$C$_6$ and undissolved NbC can be observed.

According to Little et al (1977), inhibition of grain growth can be attributed to (i) the stabilising effect of M$_{23}$C$_6$ carbides, which allows unpinning of boundaries only at high tempering temperatures. (ii) the solute drag of Nb atoms preventing migration of the boundaries during recrystallisation or grain growth. [Figs. A.3.14 - 3.16].

2.1.1.3 Temper Embrittlement in ferritic/martensitic Stainless Steel
Tempered-martensite steels are susceptible to temper embrittlement after tempering within the range 450°C-550°C or after a slow cool at similar range subsequent to a previous higher temperature tempering. The minimum in impact toughness of martensitic 12%Cr steels, classically associated with the maximum hardening between 475-500°C, is shifted towards 550°C in a commercial heat containing phosphorus, while the brittle mode of failure becomes predominantly intergranular [Lemble et al, 1979]. Phosphorus segregation to prior austenite grain boundaries has been known to influence temper embrittlement of 9-12%Cr steels [Seah and Hondros (1973)]. In the Auger electron spectroscopy work by Lemble et al (1979), it was found that nickel and chromium concentrations at the grain boundaries are larger than their nominal bulk contents. This observation is similar to that by Clausings et al (1986) reported for their work on irradiated HT-9
(12%Cr-1%Mo-W) model alloy. Phosphorus segregation to grain boundaries was induced by irradiation. However, Lemble et al concluded that phosphorus appears to be main residual element influencing the embrittlement of their alloy since its grain boundary concentration correlates well with the impairment of room temperature toughness.

Grobner (1973) associated the 475°C embrittlement of the ferritic steels to the precipitation of a chromium-rich \( \alpha' \) phase on dislocations. The 538°C embrittlement after 1000 hour, exposure time is not due to immobilization of dislocations by \( \alpha' \), but to the precipitation of carbonitrides \( M_{23}(C,N)_6 \). However, the loss of toughness after aging at this temperature is not so severe as at 427°C and 482°C and toughness shows a distinct tendency to recover after prolonged times.

Tyson (1978) in his review on kinetics of temper embrittlement described models by computer simulation of the diffusion process. He incorporated Guttman's model of interacting segregants to account for enhanced equilibrium segregation in ternary alloys.

Seah (1977) reported an equilibrium segregation of phosphorus in stainless steel and the resultant temper embrittlement.

Smidt et al (1981) reported the susceptibility of HT-9 (12%Cr1Mo-W) model alloy to temper embrittlement at 538°C after 5000 hours of ageing. This was advanced as one possible effect on the fracture toughness degradation of irradiated HT-9 alloy. Strong interactions between Ni-Sb, Ni-P, Ni-Sn and Mn-Sb can lead to cosegregation of alloy element and impurity elements at the grain boundaries. The effect of this cosegregation is the lowering of cohesion by the impurity element.
If the interaction is too strong, segregation may not occur, instead, a scavenging effect occurs as exemplified by Ti-P and Mo-P interactions in Ni-Cr steels. It is well known that Mo additions to Ni-Cr steels can eliminate temper embrittlement [Honeycombe 1981].

Briant et al (1978) in their review related the two-step temper embrittlement to the decrease in notch toughness and increase in DBTT in alloy steels after isothermal ageing in the temperature range 375°C-560°C. This same effect can be produced by cooling the steel slowly after tempering. Balajiva et al (1956 and 1959) showed that a high purity Ni-Cr steel could not be temper embrittled whereas a commercial steel of the same base composition was easily embrittled. Sb, P, Sn and As were severe embrittlers; Mn and Si were much less potent.

Low et al (1968) demonstrated that removing Ni or Cr from Ni-Cr steel decreased the embrittlement caused by Sb, Sn, P or As. Addition of Mo to Ni-Cr steel doped with P retards the two-step temper embrittlement while Mn addition enhances it. Nickel promotes segregation by con segregation mechanism. Studies by Mulford et al (1976), Ohtani et al (1976) on laboratory heats of Ni-Cr steels have shown that the grain boundary Ni concentration is directly proportional to grain boundary impurity concentration. In low carbon steels recrystallized below AC₃, the two-step temper embrittlement occurred with intergranular fracture taking place along the ferrite grain boundaries [Ohtani et al (1975)]. Evidence also exists which indicates that impurities first populate the highest energy boundaries. These are usually the prior austenite boundaries [Ogura et al (1977) and Joshi (1975)]. Parameters such as grain size, yield strength and microstructure can also influence the two-step temper embrittlement characteristics. [Viswanathan et al, 1974].
Wada et al (1976) and (1974) reported methods of reducing temper embrittlement. One method involves application of intercritical heat treatment in the \( \gamma + \alpha \) region after austenitization but before tempering. This treatment reduces the grain size by obliterating the prior austenite grains. It also reduces the yield strength and cause changes in microstructure which may affect segregation process [Wada et al (1974)]. The work of Hyzak et al (1983) on 12 Cr-1 Mo ferritic steel (HT-9) showed segregation of embrittling elements such as phosphorus to the prior austenite grain boundaries. Their Auger analyses confirm that the phosphorus segregation at prior austenite grain boundaries increases with decreasing cooling rates after austenitizing and tempering.

The role of molybdenum in phosphorus-induced temper embrittlement of 12% Cr martensitic steel was reported by Guillot, Guttmann and Dumoulin (1981).

Dumoulin et al (1980) investigated Mo beneficial effect in martensitic steels (0.2C-2.3Cr-0.8Ni-Mo). It was suggested that Mo partially inhibits the segregation of P by tying it up in the grain interior due to the strong Mo-P affinity and that Mo segregation to the grain boundaries counteracts the embrittling action of the segregated phosphorus.

Yu et al (1980) observed a similar occurrence in 2.25Cr-1Mo steels.

Speich et al (1972) reported that embrittlement at 350°C can be associated with the change in structure of carbides from \( \varepsilon \)- to cementite.
2.1.1.4 Ductile Fracture in Stainless Steels

Previous investigations by Wassilew et al (1983), Maternal Morris et al (1987), Schirra (1984), Faulkner et al (1987) on similar materials to the one under present study showed that fracture occurred by ductile mode. From these hints, it is considered useful to present a brief review of ductile fracture mechanism in this section.

McLean (1962) showed that the requirements for ductile fracture probably combine shear strain and tensile stress.

From the reports by Palmer et al (1966) and Pelloux et al (1966), the features that generally dominate ductile fracture are (i) formation and growth of holes around inclusions and (ii) concentration of shear in sharply defined bands. These processes reinforce one another: the presence of holes concentrates the strain in narrow bands emanating from the holes, [Druyvesteyn et al, 1964] while bands impinging on particles cause holes to form around these particles [Ashby (1966)]. Either of these two processes may occur first and continue the chain of events which lead to fracture.

Backofen (1964) suggested that cast and worked structures contain weak flaws which will open up under elastic loading. At the onset of yielding, slip lines will begin to extend from particle to particle [Ashby, 1966]. The particles will block the paths of the slip lines, resulting in large stress concentrations.

However, reviews by Rosenfield (1968), Ashby (1966) and Gurland (1963) highlighted the role of second phase particles such as inclusions, precipitates and dispersions, in the mechanism of fracture by ductile mode. Ashby (1966)
and Gurland (1963) reported a particle size effect on ductility. In 9-12% Cr martensitic steels, it is known that carbide particles enriched in chromium and niobium are present after heat treatment. The chromium carbides \((M_23C_6)\) and niobium carbides \((NbC)\) form as plates or triangular and disc or spherical shapes respectively [Little 1977]. According to the suggestions by Rosenfield (1968), Ashby (1966) and Palmer et al (1966), it is possible that carbide size, shape, composition, distribution and interfacial energy with the matrix affect failure mechanisms by ductile mode. An increasing ductility precedes a decreasing particle size and at very fine particles, reduction in area can approach 100% [Ashby (1966) and Gurland (1963)].

From a stress relief model by Ashby (1966), the formation and movement of a special type of dislocation (prismatic loop) can accomplish a stress-relief. These prismatic loops are comprised of vacancies and interstitial loops. Vacancy loops are formed at the particle/matrix interface in response to the residual tensile stress at the poles. As vacancy loops glide away from the particle, new loops form at the interface, thereby building up a tensile stress at the interface. An Ashby relation

\[
\sigma_T = \alpha \left( \frac{d}{\varepsilon_{\text{crit}}} \right) \lambda
\]

where \(\sigma_T\) = tensile stress
\(\alpha\) = proportionality constant
\(d\) = particle diameter
\(\varepsilon\) = strain
\(\lambda\) = distance between particle and loop
can be applied to propose the failure by ductile mode when $\sigma_T$ reaches a critical value $\sigma^*_T$, which is the stress required to cause decohesion at the particle-matrix interface.

McLean (1962) suggested that cracks which cause ductile fracture are first formed by the coalescence of dislocations. He considered the region below edge dislocation as a minute crack which can grow as a result of dislocation motion towards a pre-existing hole.

Tetelman (1967) outlined ways in which particles can assist or inhibit fracture process.

i) At small plastic strains, particles may crack or separate from the matrix [Bruckner et al (1951), Knott (1980)].

ii) A network of thin particles at grain boundary may effectively harden the boundaries and inhibit plastic relaxation around blocked slip bands and incipient microcracks [Tetelman (1967)].

iii) The particles may effectively block microcracks which have formed in the matrix, limiting their size to that of the particle spacing [Hasselman et al (1966)].

iv) The particles may block slip processes in the matrix reducing the length of dislocation pile-ups which initiate fracture [Hahn et al (1967)].

v) On a macroscopic scale, the particles may reduce the triaxial stress state around a notch if the particle-matrix interfaces are weak in shear.
Turkalo (1961) showed that particles act as corners to pin a sub-grain structure of the same size as the interparticle spacing. Embury et al (1966) showed that the flow stress varied as the reciprocal square root of subgrain size.

Models by Smith and Barnby (1967) related cavity nucleation to applied strain - in terms of an infinite series of dislocation pile-ups each of length of d, blocked by particles of radius c. As the matrix strain (or the number of dislocations in each pile-up) is increased, the stress on the particle/matrix interface also increases until eventually a Griffith fracture criterion is obtained and the interface decoheres.

According to Knott (1980), shear fractures in quenched and tempered steels appear to run from carbide to carbide, decohering the carbide/matrix interfaces, rather than cracking the particles. Such decohesion can occur either by direct effect of the applied stress or from local stresses induced by arrays of dislocation tangles around the particles. During plastic straining of a matrix containing carbides, dislocations will pile up producing work hardening by the Orowan type of mechanism. As plastic strain is increased, dislocation induced stresses build up around the carbide particle and the particle/matrix interface. At a critical strain, the interface (or particle) fractures.

The critical stage can be expressed as

\[ nb = 2\sqrt{2d \left\{ (1-V^2)\gamma/\pi c E \right\}^{1/2}} \]

where \( n \) is the number of dislocations of Burgers vector \( b \) in each pile up, \( E \) is Young's Modulus, \( v \) is Poisson's ratio, \( \gamma \) is the interfacial work of fracture, \( c \) is the particle
radius and \( d \) is the length of dislocation pile-up: [King and Knott (1981)].

Knott et al (1975), (1977), and (1981) proposed ductile failure by zig-zag mechanism. Alternate ridges and valleys with major inclusions eg. MnS, situated at the troughs and peaks were observed. He associated ductile fracture with void growth around inclusions and precipitates eg. MnS and carbides.

2.2.5.0 Segregation of solute elements

The earlier works of Gibbs showed that a differential change in specific interfacial energy can be related to variables such as excess interfacial entropy, interfacial adsorptions, chemical potentials of solute and solvent, and the absolute temperature [J.W. Gibbs collected works pp. 219-330].

McLean's model of equilibrium segregation states that, for an impurity with binding energy to the lattice, \( E_b' \), at any temperature, \( T \), there will be an increased concentration of that impurity in a monolayer on boundaries and interfaces, \( C_b \). The driving force for this is the reduction of energy, \( E_b \) of the impurity on placing it, in a strain-free environment, on the grain boundary. \( C_b \) is given by the relation

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

where \( C_g \) = concentration of impurity in the matrix

and \( K = \) Boltzmann's constant
Extension of these ideas to account for time required to accumulate the monolayer leads to a modified relation

\[ \frac{C_x - C_i}{C_b - C_i} = 1 - \exp\left(\frac{4D_i t}{\alpha^2 d_i^2}\right) \text{erfc}\left(\frac{4D_i t}{\alpha^2 d_i^2}\right) \]

where

- \( D_i \) = diffusivity of the impurity in the matrix
- \( C_x \) = concentration of impurity on the boundary after time \( t \)
- \( \alpha = \frac{C_b}{C_i} \)
- \( d_i \) = boundary width \((2.5 \times 10^{-10})\)
- \( t \) = time

Anthony (1969) in his model showed that if the binding energy of vacancy-solute complex is much larger than the thermal energy \( \frac{3}{2}kT \), and if the complex is relatively mobile, then, solute enrichment of vacancy sinks and solute depletion of vacancy sources will occur from vacancy flow. Factors that control non-equilibrium segregation include solute and solvent diffusivities, the magnitude and extent of the vacancy gradient, the magnitude and sign of the binding energy for vacancy-solute complex and the total flow of vacancies.

Faulkner (1981) combined McLean's modified equation for equilibrium segregation with another equation he developed from ideas of Aust and Westbrook (1967) and Anthony (1969) for non-equilibrium segregation to propose a combined model of equilibrium and non-equilibrium segregation [Faulkner 1987a]. Non-equilibrium segregation depends upon the creation of vacancy concentration gradients in the neighbourhood of vacancy sinks during fast cooling from a high temperature, \( T_1 \). Vacancies dragged down this gradient will also pull impurity atoms with them, if there is any interaction between them.
If the attraction between vacancy and impurity is very strong, considerable amounts of impurities will build up at effective sinks in the microstructure. The concentration of impurity, \( C_x \), at a given distance, \( x \), from an interface after an effective time, \( t \), can be written as

\[
\frac{C_x - C_g}{C_b - C_g} = \text{erfc} \left( \frac{x}{2(D_v t)^{1/2}} \right)
\]

\( C_b \) can be calculated from relation

\[
\frac{C_b}{C_g} = \exp \left( \frac{E_b - E_f}{kT_i} - \frac{E_b - E_f}{kT_{0.5} T_m} \right)
\]

\( E_b \) = vacancy-impurity binding energy (Chapman et al, 1983)

\( C_b \) = concentration of impurity on interface of free surface

\( C_g \) = concentration of impurity away from interface

\( T_i \) = starting solution treatment temperature

\( T_{0.5} T_m \) = temperature at which diffusion is assumed to cease

\( E_f \) = vacancy formation energy

\( D_v \) = diffusion for vacancy-impurity complexes in the matrix

In order to account for effective time, an expression involving the quenching rate, \( \Theta \), and solution treatment temperature, \( T_i \), can be written as

\[
t = \frac{RkT_i^2}{\Theta E_A}
\]

\( R \) = constant (~0.01)

\( E_A \) = average activation energies for diffusion of the impurities and the vacancies in the matrix
A critical time, $t_c$, which is dependent upon grain size, $d$, of the crystalline solid, and relative diffusion rates of the impurities, $D_i$, and vacancy-impurity complex, $D_v$, is suggested as a cut off limit.

$$t_c = \frac{D_v d^2 \ln(D_v / D_i)}{4(D_v - D_i)}$$

$\delta = \text{constant (5 x 10}^{-2})$

At any time $t > t_c$, the impurity flux ceases, and desegregation can occur. The desegregation equation can thus be written as

$$\frac{C_x - C_g}{C_b - C_g} = \left(\frac{D_v}{D_i} t\right)^{\frac{1}{2}} \exp\left(\frac{-x^2}{4D_i t}\right)$$

Obtaining values of $C_x$ from both equilibrium and non-equilibrium equations, a net amount of segregation can be deduced from relation

$$F = \frac{C_x(ES)}{4} + C_x(NES)$$

$F$ is the total segregation concentration, less concentration contribution from the existing matrix level $C_g$.

$C_x(ES)$ is assumed to be a monolayer segregation extending out 2.5Å into the grain adjacent to the boundary. The concentration level corresponding to this, from the same amount of segregation, in a 10Å wide zone adjacent to the boundary is $C_x(ES)/4$.

For the $C_x(NES)$, values were obtained at 100Å intervals. It is then assumed that segregated zones will commonly extend out to 100Å. Therefore, 10 values of $C_x(NES)$ are
summed to give an effective integration of the NES concentration profile $C_\text{NES}$, The average concentration at these ten points is multiplied by 10 to yield the effective concentration; should all of the segregant be located in the 10Å wide zone being considered. This model has been tested experimentally on a ferritic/martensitic steel (1.4914) solution treated at 1080°C and quenched at varied cooling rates. It was predicted that maximum segregation of silicon occurred at 20°C per second cooling rate after solution treatment at 1080°C [Faulkner 1987a].

The kinetics of segregation in a binary system have been treated by McLean (1957) and applied by Seah (1977) without modification to explain data presented by Carr et al (1953) on segregation in a multicomponent alloy.

Guttmann (1976) and Tyson (1978) investigated segregation kinetics in ternary systems, taking into account the coupled diffusion of segregating elements due to their interactions within the grain boundary layer. They concluded that segregation in both binary and ternary systems occurs much more rapidly than predicted by the well known McLean relation.

Joshi (1978) used AES to evaluate the role of interface impurities in the failure of materials. In most of the systems studied, he reported, solute segregation occurring in narrow regions at grain boundaries. The segregant either decrease the fracture surface energy of the material or lower the plastic strain energy associated with fracture or both, thereby weakening the interface. His report showed that solute-hydrogen interactions predominate in some alloy systems, thereby possibly accelerating the penetration of hydrogen along grain boundaries and causing a subsequent embrittlement. Suzuki (1962) reported segregation of solute atoms to stacking faults in α-brass.
with 30% Zn which was melted from 99.99% Cu and 99.9% Zn. The free energy of a stacking fault in a solid solution is a function of the solute concentration. Since this solute concentration at the stacking fault is not the same as that of the surrounding perfect region, when the material attains thermal equilibrium, an effect on the free energy of stacking fault is possible.

Kasen (1983) reported additional evidence that a major source of grain boundary segregation is solute acquisition by migrating boundaries during recrystallisation and grain growth.

Chapman et al (1983) developed a computer model to simulate grain boundary segregation during quenching from high temperatures. In this model; the impurity atom was assumed to have three basic energies associated with it, which are

(i) vibrational or kinetic energy at all temperatures above absolute zero
(ii) Elastic strain energy,
(iii) surface/interfacial energy due to any electronic chemical, and dimensional mismatches between the impurity atom and the surrounding matrix. These ideas were used to quantify the energetic interactions which influence vacancy-impurity complex movement. It was suggested that prior heat treatment has considerable influence on the extent and magnitude of grain boundary segregation and, hence, on material properties. Their A.E.S. result indicated the presence of boron and phosphorus segregation at prior austenite boundaries in a tempered 12% Cr martensitic steel.

Westbrook (1969) in his review, highlighted problems encountered in applying varieties of mechanisms of segregation to embrittlement phenomena at or near prior austenite grain boundaries.
Yoo, White and Trikaus (1985) investigated the effects of interfacial solute segregation on creep ductility in terms of its effects on interfacial energies and diffusivities. They discussed interfacial energies for the case of very slow fracture at high temperatures where equilibrium of the solute is maintained throughout the fracture process. At the intermediate temperatures \((0.4-0.7)T_m\) and low strain rates \(<10^{-4}\text{s}^{-1}\), the shear stresses at inclined boundaries are relaxed by grain boundary sliding, which leads to inhomogeneous stress concentrations at non-planar irregularities on the grain boundary. Their two-component nucleation model, which treats the effect of interfacial segregation on intergranular cavitation directly, shows that the steady-state nucleation rate is increased 4 to 6 orders of magnitude by non-equilibrium segregation.

Tipler and Hopkins (1976) claimed that the embrittling effects of trace elements in ferritic steels are the same as those observed in copper to which antimony has been added.

Doig and Flewitt (1981) reported segregation of Cr to prior \(\gamma\)-boundaries during quenching of \(2\frac{1}{4}\%\) Cr \(1\%\) Mo steel. Chromium segregated to grain boundaries via non-equilibrium segregation mechanism. Various techniques have been used to determine segregation.

Williams et al (1976) reported segregation of boron to grain boundaries in solution treated type 316 austenitic steel.

Karlsson and Norden (1988) used a combination of techniques, eg. TEM, FIM, AP and IAP to study boron grain boundary segregation in austenitic stainless steels of types 316L (40 ppm or >1 ppm boron) and "M_o free 316L" (23 ppm boron). Boron segregation behaviour was mainly of the non-equilibrium type after cooling from 1075 or 1250°C whereas equilibrium segregation dominated after rapid cooling from 800°C. They related segregation of boron to misorientation characteristics of grain boundaries. Amount of non-equilibrium segregation was small for general boundaries and no segregation was detected at coherent twin boundaries.

Bercovici et al (1970) used the ideas of Aust et al (1967) to explain composition gradient in the vicinity of the grain boundary. They proposed mathematical models involving misfit of solutes and/binding energy.

Reviews of segregation theory via equilibrium mechanism were presented by Seah and Hondros [(1973) and (1977)]; and Guttman (1976). Seah and Hondros (1977) associated phosphorus segregation to temper embrittlement phenomenon in stainless steels.

Molybdenum segregation to grain boundary has the same influence on the segregation of Cr as it had on that of P since it decreases both the amount of segregated Cr and its temperature dependence. Guillon, Guttmann and Dunmoulin (1981) reported that Cr segregation was a maximum in their M_o-free material embrittled at 500°C. In this same material P segregation was highest.
Kinsman and Aaronson (1967) associated the acceleration of ferrite reaction to the segregation of Mo to the interface, giving rise to an impurity drag effect. Hillert (1968) supported this view but by somewhat different reasoning.

2.3.6.0 Radiation Damage in Ferritic/Martensitic Steels

It is considered important to present a brief review of radiation damage in ferritic steels since the present study involves investigation of effects of radiation on high temperature mechanical property. The work of Alexander (1986) described in details, radiation damage features in ferritic steels.

However, it is known that radiation damage in stainless steels occurs through primary collisions that suddenly give individual atoms large amounts of kinetic energy. The nature of the primary interaction and the energies imparted depend on the kind of radiation. For instance, high energy neutrons and charged particles can cause defects such as vacant lattice sites, interstitial atoms and transmutted atoms when they interact with stainless steel. Energetic neutrons can penetrate large distances into steels and upon collision, transfer sufficient energy to the steel atoms, hence dislodging them from their inherent lattice positions. They can also interact with certain alloying components of steel to cause transmutation reactions [Harkness et al (1969), Barnes et al (1965)]. For example, energetic neutrons can interact with boron and nickel in ferritic steels to produce helium gas atoms via \( (n,\alpha) \) reactions [Schroeder (1987), Wassilew (1983) and Alexander (1986)]. In a thermal reactor, neutrons with energies between about 0.1 and 10 MeV are produced by the fission process.
process. Neutrons with intermediate energies (10eV to 0.1MeV) are created by the elastic scattering of fission neutrons from atoms of materials containing low atomic weight elements such as carbon and hydrogen. These materials, referred to as moderators, are embodied in the reactor core in order to slow down neutrons and sustain the fission process. Neutrons eventually attain energies equivalent to the thermal vibrations after interaction with atoms in the moderator material. These type of neutrons are known as thermal neutrons with energy of ~0.025eV at 20°C. [Little et al 1976].

Smith (1956) first observed the effect of fast neutron irradiation on impact properties of ferritic/martensitic steels.

From the work of Seeger (1957) it was reported that recovery of neutron induced changes in hardness and strength occur within approximately the same temperature range as recrystallization of strongly cold worked steel.

Several workers [Rawls et al (1980), Gelles (1982), Anderko (1980), Butterworth (1982) and Little (1979)] have investigated the effects of neutron irradiation on 9-12% Cr ferritic/martensitic steels at varied temperatures.

Gelles et al (1983) reported development of voids and dislocation loops after irradiation of 12% Cr-1 Mo (HT-9) steel. The highest swelling rate obtained for the material is ~0.25% per 10^{22} n cm^{-2} i.e. one twentieth the swelling rate expected for austenitic steel.

Little et al (1980) observed unusual spatially heterogeneous dislocation structures, comprising, colonies of dislocation
loops, with a \textless100\textgreater Burgers vector, interspersed within a matrix, of high network of dislocation density, in irradiated Fe-11\% Cr-M\textsubscript{0}V Nb steel (FV44B).

Eyre and English (1974) studied defect structures in fcc and bcc metals irradiated at low temperatures. Their report suggests that the preferred attraction of dislocations, including loops, for interstitial point defects played important role in the sense that it leads to more stable interstitial loops than vacancy loops during irradiation. The geometry of vacancies influence their survival when they interact with other point defects.

Boothby and Williams (1981) from their work on 12\%Cr-13\%Ni steel irradiated with Ni\textsuperscript{6+} ions in Harwell Variable Energy Cyclotron, showed that 12\%Cr-13\%Ni steel transformed from austenite matrix to a predominantly bcc structure with Ni\textsubscript{3}Si precipitate at voids and dislocation loops.

Kawanishi et al (1985) reported no cavity formation or saturation of dislocation density after irradiation to 30 dpa of their material (9Cr-2Mo steel).

2.3.6.1 Calculation of the number of displacements per atom
In this present study, it is expected that displacement damage will occur as a result of irradiation at 650\textdegree C. It is also expected that helium gas will be produced via \textit{(n, α)} reaction due to high energy neutron interaction with boron and nickel in ferritic/martensitic steel. It will be very useful to survey the theory involved in the calculation of number of displacements per atom.
Firstly, the number of neutrons striking the material in the reactor, should be evaluated. Since the neutrons are not mono-energetic, the integral flux or total flux of neutrons of all energies will be appropriate.

\[ \Phi = \int_0^\infty \phi(E) dE \text{ (n cm}^{-2}s^{-1}) \]  \hspace{1cm} 2.3.7.1

The time-integrated flux is then

\[ \int_0^t \phi(t) dt \text{ (n cm}^{-2}) \]  \hspace{1cm} 2.3.7.2

If flux is constant with time, then

\[ \int_0^t \phi(t) dt = \Phi t \]  \hspace{1cm} 2.3.7.3

Consider the number of interactions between the neutrons and the atoms in the alloy. This can be written as

\[ \frac{N_r}{N_0} = \int \phi(E) \sigma(E) dE \]  \hspace{1cm} 2.3.7.4

but for monoenergetic neutrons \( \frac{N_r}{N_0} = \Phi \sigma \) \hspace{1cm} 2.3.7.5

where \( \frac{N_r}{N_0} = \text{fractional number of interactions per second} \)

\( \Phi = \text{neutron flux (n cm}^{-2}s^{-1}) \)

\( \sigma = \text{microscopic cross section, a measure of the probability per neutron of an interaction (cm}^2) \)

\( (10^{-24} \text{ cm}^2 = 1 \text{ barn}) \)

Assuming hard sphere elastic collision theory for collisions between neutrons and lattice atoms, the maximum energy transferred when a particle of mass \( m_1 \) and energy \( E \), strikes a particle of mass \( m_2 \) at rest is given by
For mass of neutron = 1

\[ E_{\text{max}} = \frac{4m_1 m_2}{(m_1 + m_2)^2} E_1 \]  

\[ E_{\text{max}} = \frac{4E_1}{A_2} \]

Where \( A_2 \) is the mass number of the struck atom. If the energy transfer to the struck atom exceeds some threshold value, (~25eV), the atom will be displaced from its lattice site. Such an event is called a primary knock-on (PKO) and will interact with other lattice atoms in its vicinity, thereby displacing some of them before coming to rest.

Kinchin and Pease (1955) model was based on the following assumptions:

(i) hard-sphere scattering,

(ii) Inelastic energy losses occur only above a threshold energy \( L_c \)

(iii) no crystallographic effects

(iv) no recombination of point defects. The number of displaced atoms (vacancy-interstitial pairs) \( N_d \) produced per collision by a PKO of energy \( E_p \) can be written as

\[ N_d = \frac{E_p}{2E_d} \text{ for } 2E_d < E_p < L_c \]

\[ = \frac{L_c}{2E_d} \text{ for } E_p > L_c \]

Nelson and Nelson et al (1969, 1972) in their modification of Kinchin and Pease model incorporated correction factors for assumptions (i), (ii) and (iii). Hence, the model by Lindhard et al (1963) was applied to obtain fractional energy lost in elastic collisions while data from studies of Beeler and Besco (1964) was used to obtain a correction for channelling. The computer simulations of the cascade
process carried out by Torrens and Robinson (1972) provided evidence to support the modified Kinchin and Pease equation

\[ N_d = \frac{k(E_p - E_i)}{2E_d} = \frac{kE_{\text{Damage}}}{2E_d} \]  

where \( E_p \) = energy of PKO, \( E_d \) = threshold displacement energy \((\approx 25\text{eV for metals})\), \( E_i \) = inelastic energy loss, \( E_{\text{Damage}} \) = Energy available for displacement, \( k \) = displacement efficiency \((\approx 0.8)\)

Norgett (1971) found that the simulation is in agreement with earlier dynamics studies by selecting a value for \( E_d \) of 37eV (Erginsoy et al, 1965).

The model according to Torrens-Robinson-Norgett (1972) observations has been adopted as the IAEA standard for estimating \( N_d \) (TRN standard).

From here, \( k = 0.8 \); \( E_d = 40\text{eV} \) in eq. 2.3.7.8 will give \( N_d = 10E_{\text{damage}} \)  

where \( E_{\text{damage}} = E_p - E_i \) (Lindhard 1963)

The number of neutrons-atom collisions \( C \) per atom in unit time due to a monoenergetic flux \( \Phi \) of neutrons of energy \( E_0 \) can be written as

\[ C = \Phi \sigma (E_0) \]  

The total number of displacements produced per atom in unit time in a metal subjected to a neutron energy spectrum \( \Phi(E) \) can be written as : -
I = \int \sigma(E) N_d(E) \phi(E) dE \quad 2.3.7.9b

[Little, 1976]

2.3.6.2 Irradiation Effect on microstructure in ferritic/martensitic steels

This section gives a brief survey of irradiation effects on microstructure in ferritic/martensitic steels and its relation to high temperature mechanical behaviour. Since the present study includes irradiation works, it is worthwhile to present this review.

Major irradiation effects on mechanical properties of ferritic/martensitic steels include (i) variation in tensile yield strength, (ii) variation in hardness, (iii) variation in work hardening rate and (iv) variation in ductility. An important parameter is the ductile-to-brittle transition temperature (DBTT) which describes the extent of irradiation damage in ferritic/martensitic steels. A relationship can be proposed between fracture energy and the transition temperature. If the temperature is increased through the transition, the fracture energy will increase until it reached a constant value. This region of constant fracture energy can indicate the extent of irradiation-induced embrittlement.

Little et al (1982) reported heavy precipitation along grain boundaries in 12 Cr steels after fast neutron irradiation. It was suggested that precipitates along grain boundaries are directly inhibiting dislocation motion. Solute element interactions with vacancies and exhibition of high binding energies can oppose shrinkage processes, and hence, vacancy clusters of smaller sizes that can be annihilated at sinks may be retained.
Smidt and Sprague (1972) reported copper (−0.05–0.35 wt%) as a sole substance for the severe 288°C radiation embrittlement in pressure vessel steels at doses in the order of 1–2x10^{19} n cm^{-2}.

Nickel in A533B (0.4–0.7%), A508 (0.5–1 wt%) and phosphorous (−0.015–0.03 wt%) are other alloying elements that have contributions to initiation of radiation embrittlement. However, phosphorus level less than 0.01% in ferritic/martensitic steels has eliminated serious problems in PWR vessel materials.

Little (1976) reported that vacancy and interstitial cascades play some role in irradiation-induced embrittlement. It is known that vacancy and interstitial point defects are dispersed to form displacement spikes along the primary knock on track. A central core of vacancies with the associated interstitials distributed at the periphery will form. These arrangements in the spikes can encourage a subsequent collapse of the central core to form loops. These loops when immobile can act as strong barriers to dislocation motion, and hence, initiate irradiation hardening. Pronounced hardening of the matrix can weaken the interface and embrittlement can occur.

Irradiation hardening and embrittlement has been associated with neutron dose in a relation (Φt)^n, for experimental n-values in the range 0.31–0.43. According to dispersed barrier models of irradiation strengthening, n can be assigned a value of ~0.5. It is assumed that the rate of creation of dislocation obstacles per unit volume increases linearly with neutron dose. The production of helium gas via (n, a) reactions is another consideration to explain radiation-induced embrittlement.
Goodhew et al (1986) and Schroeder (1987) reported that helium gas atoms agglomerate to form bubbles on grain boundaries and initiate intergranular fracture by cavity growth.

Irradiation work on 9-12 Cr ferritic/martensitic steels carried out by several workers, [Harries (1983), Klueh et al (1981), Gelles (1982), Stamm et al (1987) and Wassilew et al (1983)] showed irradiation enhanced increases in hardness, tensile strength and reductions in tensile elongations to fracture at both room and higher temperatures.

Klueh et al (1981) investigated HT-9 (Fe-12Cr-1Mo steel) irradiated at 50°C to a dose of 9.3 dpa and injected <82 ppmHe. Their result showed that the changes in properties are entirely due to the displacement damage and that no significant high temperature irradiation embrittlement due to helium bubbles can be observed.

Klueh and Vitek (1983) reported that the 700°C tensile ductilities of HT-9 base steel (12 Cr-1-Mo) with and without additions of <2% Ni are relatively unaffected by irradiation at about 50°C to <42 ppmHe.

Anderko (1980) and Wassilew et al (1983) from their post irradiation tensile and creep rupture tests data supported observed transgranular fracture mode.

Faulkner and Anderko (1983) suggested that ferritic/martensitic steels have inherently high resistance to intergranular fracture due to their high stacking fault energy, a large difference between surface and grain boundary energies and finer effective grain or lath size. Wassilew (1983) explained that absence of twin boundaries in ferritic/
Martensitic steels provide no vacancy source for the growth of small helium bubbles observed on lath and prior austenite boundaries in irradiated 9-12 Cr ferritic/martensitic steel. He associated small bias of edge dislocations in ferritic-martensitic steels with a lower-net vacancy concentration, and hence, a reduced vacancy flow into helium bubbles on lath boundaries.

Little et al (1979) reported that the impact properties of irradiated 12% Cr steels showed increases by 40° to 60° of impact transition temperatures and reduction in upper shelf energies by ~ 0.125 J/mm² after thermal reactor irradiation of FV448 (Fe-11Cr-Mo V Nb) steel at 300°C. Irradiation at 450°C and 500°C indicate no significant changes in impact properties observed.

Hawthorne et al and Smith et al (1981) investigated a Charpy v-notch specimen of HT-9[Fe-12Cr-1Mo] steel irradiated to ~5 dpa at ~420°C. Their results showed that 41J transition temperature is increased by approximately 100°C and that the upper shelf energy at 150°C is reduced from 150 to 88J. Combined effects of irradiation hardening and temper embrittlement similar to that observed after thermal ageing of unirradiated steel at 538°C was taken as responsible.

Gelles et al and Hu (1982) reported large increases in transition temperatures after irradiation of HT-9 [12Cr-1Mo] steel at 390°C. It was suggested that hardening due to G-phase (Ni₃Si) formation and embrittlement following higher temperature irradiation associated with precipitation in α-ferrite stringers are responsible. Kayano et al (1983) studied irradiation embrittlement of neutron-irradiated ferritic/martensitic steel. They observed that irradiation caused reductions in toughness and DBTT of their
9 Cr - 2 Mo steel. It was noted that the DBTT difference between the irradiated and unirradiated specimens decreases with increasing concentration of martensite.

2.3.6.3 Combined Irradiation and high temperature effects


Little et al (1982) observed temperature variation of radiation hardening and explained the phenomenon on the basis of the change in loop size and density with temperature through the relationship \( \Delta \tau = 2\mu b f(d, N) \); where \( \Delta \tau \) is the shear stress increase resulting from glide dislocations with an array of dislocation loops, \( N \) is the loop density, \( d \) is the loop diameter, \( \alpha \) is a factor proportional to the obstacle length, \( \mu \) and \( b \) are the shear modulus and Burgers vector respectively. The term \( f(d, N) \) can be expressed in form \((dN)^{1/3}\) (Friedel, 1964) or \(dN^{2/3}\) (Kroupa and Hirsch 1964). He suggested that second order effects comparable to the super imposed matrix softening may be responsible.

Wassilew (1983) proposed that large ductility increase observed in ferritic/martensitic steel (1.4914) irradiated at elevated temperature could be due to thermal effects. Softening processes can be rationalised in terms of decreases in network dislocation density of the martensite matrix. This could be brought about by both irradiation-induced recovery and thermal effects.
In an FV448 steel (Fe-11Cr-MoVNb) irradiated by fast neutrons at 615°C, Little et al. (1982) reported clear evidence for sub-grain formation and dislocations predominant presence within sub-grain boundaries. Softening effects can be advanced alternatively in terms of recovery-induced increases in sub-grain size, $d$, since the substructure strengthening component can also be expressed in terms of a Hall-Petch expression as proportional to $d^{-n}$ where $n$ has a value between 0.5 and 1 [refs. 45 and 46 in Little et al. (1982)].

The rapid rates of dislocation climb induced by the high non-equilibrium concentrations of point defects generated during irradiation can play some role in the lowering of the initially high dislocation densities of the tempered martensite. Also, variation in precipitate distribution induced by irradiation and irradiation-induced precipitate reactions due to depletion of strengthening elements, e.g. silicon, nickel and molybdenum, from the lattice can contribute to softening of the tempered martensite matrix.

2.3.6.5 Radiation-Induced Segregation (RIS)
Radiation-induced segregation is a phenomenon that has attracted greater attention in recent years. (BNES Conf. October 1987; ICFRM - 3 Oct. 1987; Berkeley Nuclear Laboratory Symposium, Sept. 1986).

Several workers including Anthony (1972), Johnson and Lam (1976), Wiedersich et al. (1983), Okamoto and Wiedersich (1974), Perks et al. (1986), Murphy (1986); Mahon et al. (1986); Takahasi et al (1987); Watanabe et al (1987), Ohnuki et al. (1987) and Williams (1982) have reported various approaches to explain RIS Processes.
Dynamic redistribution of alloy components with net gradients on interfaces can affect many physical and mechanical properties. [Piller and Marwick (1977)]. Effects associated with RIS include sensitisation of nuclear reactor core component materials [Taylor 1986]. These effects can be more serious in fission and fusion nuclear reactors core components.

Large point defects produced in these components material, during irradiation, enhanced RIS. A well documented review by Wiedersich and Lam (1983) explored various mechanisms of RIS processes. RIS mechanisms are based on the main point defects (vacancies and interstitials) interactions with alloy components. RIS occurs when the fluxes of specific alloying elements are preferentially coupled to persistent fluxes of point defects. [Anthony 1972]. The vacancy and interstitial mechanisms are based on inverse Kirkendall effect. From reports by Smilgalskas and Kirkendall (1947), it was suggested that composition gradient of alloy component can induce a net flux of point defects across a 'marker plane'. During irradiation, defect fluxes are generated and it can be expected that the inverse Kirkendall effect can occur at temperatures where defects are mobile. Hence, a gradient defect concentration can induce a net flux of alloy components across a 'marker plane'. Interaction of solute elements and defect fluxes may result in the formation of defect-solute complexes. When the sum of the defect-solute binding energies $E_b(d-s)$, and the defect migration energies $E_m(d)$, exceeds migration energy of the complex $E_m(d-s)$, the defect-solute complexes will be mobile.

$$E_b(d-s) + E_m(d) > E_m(d-s)$$  \[2.3.7.1\]

These mobile defect-solute complexes as distinct entities can diffuse down their own concentration gradient. When
the direction of flow of these complexes is the same as for defect fluxes; it becomes likely, that solute atoms can be swept towards defect sinks in initially homogeneous alloys. Johnson et al (1976) and Wiedersich et al (1977) predicted binding energies of, >0.2eV for effective defect-solute complex activity.

An interstitial-induced inverse Kirkendall effect is not certain. Lack of details about partial diffusion coefficients due to interstitial is included in reasons advanced.

However, Rehn and Okamoto (1983), based on general idea of misfit, favour an interstitialcy mechanism in their work on Ni-Si, Ni-Al and Ni-Al-Si alloys. The migration of interstitial-atom complexes is thought to be important for the RIS of alloy components with a large size mismatch. Lack of data on binding energies of interstitials with major elements make it more uncertain for RIS via interstitialcy route. Generally, undersized solutes are expected to be enriched at an effective sink while the oversized atoms are to be depleted. An exception to this rule are the Ni-Ge and Al-Ge systems where oversize solute are enriched at sinks.


Lam et al (1978) studied RIS in heavy ion bombarded dilute Ni-base binary alloys. They predicted, theoretically, spatial redistribution of undersize solute silicon in nickel during 3 MeV and 75 eV Ni⁺ ion bombardment. Their experimental profiles obtained from AES and SIMS techniques show
a temperature dependence of RIS. Little segregation can be observed below 500°C and above 660°C. Significant surface precipitation of the new $\gamma^1$(Ni$_3$Si) phase can occur at intermediate temperatures.

Okamoto et al (1974) observed RIS in 18Cr-8Ni-1Si steel; commercial 316L, Vanadium and Nickel under electron irradiation. Their interpretation of the data agree with that of Anthony (1972). It can be noted that concentration up to 7% nickel was observed at least 1200Å from the interface compared to the nominal alloy composition of 0.58% Ni.

Brimhall (1984) suggested that the large difference between diffusion coefficients for impurities in ferritic and austenitic matrices seems a much more likely reason for the difference in behaviour of Ni and Cr during segregation in γ- and α- steels.

Clausing et al (1986) used AES to study RIS on lath boundaries in neutron irradiated HT-9. They found that P, Si and Cr segregated to lath and lath packed interfaces at 408°C. Chromium depletion was observed at 519°C. No significant segregation was observed in the ductile regions of the fracture surfaces at this temperature.

Gelles (1983) showed that G (Ni$_3$Si) phase dissolves above 500°C in ferritic/martensitic alloys. This partly explains the more ductile behaviour of this material.

If the potential segregation is spread more thinly over a larger interfacial area, then this is an indirect evidence of segregation-induced ductility loss or brittle fracture. This idea can be deduced from evidence that the improved post irradiation ductility of HT9 over austenitic alloys is
due to the presence of much higher density of lath and lath packet interfaces [Faulkner and Anderko 1983].

The work of Ohnuki et al (1987) showed the effect of injected helium on RIS concentration. Molybdenum enrichment of grain boundaries in SUS316 material was reported. The presence of helium suppressed the enrichment of nickel and chromium on grain boundaries. However, silicon concentration remained constant but molybdenum and manganese concentration are slightly increased on the grain boundary. RIS produces, not only large compositional difference, but also cause transformational changes. [Ohnuki et al (1981)].

Packan et al (1986) in their tensile experiment on Ni-8 at, %Si irradiated to 0.1-0.3 dpa with either 7MeV protons or 28MeV α-particles at 750°C, reported RIS of silicon giving rise to Ni₃Si layers at internal and external surfaces. Their data showed that all irradiated specimens exhibit good ductility and failure was mainly transgranular. They concluded that RIS of silicon can not be associated with intrinsic embrittlement. However, Bajaj et al (1981), Yang (1982); Vaidyanathan (1982) reported serious tensile ductility degradation by silicon segregation for Fe-Ni base alloys after neutron irradiation. Layers of continuous γ¹ structure, enriched in Ni, Ti, Si and Nb, present on the grain boundary were associated with embrittlement. It was suggested that G (Ni₃Si) phase is not an inherently brittle phase but its complement Ni₅Si₂ can be a severe embrittler.

Piller and Marwick (1977) reported segregation of silicon to both external and internal sinks in irradiated nickel alloy. They ascribed the relatively rapid diffusion of silicon-normally substitutional in nickel to an interstitialcy mechanisms.
Kenik (1976) observed segregation of silicon to faulted interstitial loops during 4MeV Ni$^+$ ion irradiation at 517°C and 677°C in the LSI steel containing 1.05% Si.

Barbu and Ardell (1975) in their report, showed that precipitation of Ni$_3$Si during 500keV Ni$^+$ ion irradiation of Ni (Si) alloys at 500°C is due to the nucleation of precipitate at interstitial loops. They attributed the necessary increase in silicon concentration to the migration of silicon-interstitials to the loops.

Mahon et al. (1986) detected chromium segregation in the temperature range 350-650°C, with a peak at 550°C in a series of ferritic 12% Cr binary alloys under heavy ion and electron irradiations to doses of 10 dpa. Enrichment of nickel, silicon and phosphorous were detected on defect sinks.

2.3.7.0 Heat loss from a rectangular section plate

It is considered necessary in this section to explore theoretical background of heat transfer, since quenching rate determination using theoretical model is part of this present study. This review will highlight various parameters employed at all stages of calculation and form the basis upon which experimental data has been assessed.

In order to quantify heat loss from quenched material, parameters such as thermal conductivity of the material, surface area of section place, heat coefficient due to material and boundary layer are involved.
The rate of heat transfer between a fluid and a wall or solid boundary can be expressed as

\[ \dot{Q} = -UA(T_s - T_w) \]  

\( \dot{Q} \) = rate of heat transfer (J/S)
\( A \) = surface area of solid (m²)
\( T_s, T_w \) = free stream and solid boundary temperatures respectively

To obtain \( U \), the relation

\[ \frac{1}{U} = \frac{x}{k} + \frac{1}{h} \]  

2.3.8.2

can be employed.

where
\( x \) = effective thickness of sample (m)
\( k \) = thermal conductivity of the material (J/S/m²K)
\( h \) = convection or film coefficient (J/S/mK)

In case of heat transfer due to convection, there are three approaches.

i) Assuming the fluid adheres to the solid boundary and hence, consider heat flow by conduction. In this method, one would need to find the temperature gradient in the fluid at the closest proximity to the solid surface boundary.

ii) Reynold analogy between fluid friction and heat transfer.

iii) Principle of dynamic similarity with a dimensional analysis for correlation with empirical data.
Using the third approach involves four dimensionless factors which are important in heat flow expressions.

\[ \text{Nu} = \frac{hL}{K} = \phi \text{Pr}^m \text{Re}^n \text{ Nusselt number} \quad 2.3.8.3 \]

\[ \text{Pr} = \frac{\mu C_p}{K} \quad \text{Prandtl number} \quad 2.3.8.4 \]

\[ \text{Re} = \frac{\rho U L}{\mu} \quad \text{Reynold number} \quad 2.3.8.5 \]

\[ \phi = \text{constant of proportionality} \]

\[ L = \text{critical dimension (m) or gauge length in this present study} \]

\[ K = \text{Heat conductivity of fluid (J/S/m°C)} \]

\[ \rho = \text{Fluid density (Kg/m}^3) \]

\[ \mu = \text{Fluid viscosity (Kg/ms)} \]

\[ U = \text{Fluid flow velocity (m/s)} \]

\[ C_p = \text{Heat capacity of fluid (J/Kg °C)} \]

In the quenching experiment, the third approach can be applied for natural convection (air, oil and water quenching). In this case, the fluid flow is the result of heat transfer from the hot body. As temperature gradient develops across the thermal boundary layer and fluid surface; fluid expansion occurs in that region and the fluid becomes less dense. This less dense fluid region will rise and cooler fluid will replace it at the solid/fluid interface. This process continues until the solid boundary is at room temperature.

In order to determine whether the flow is laminar or turbulent, knowledge of factors such as the Grashof and Prandtl numbers are used for the case of natural convection flow.
Gr (Grashof number) = $\frac{\rho^2 \Theta L^3}{g \mu^2}$ \hspace{1cm} 2.3.8.6

$\Theta$ = fluid/wall temperature difference  
g = force of gravity  
Gr = dimensionless Grashoff number

From equations 2.3.8.3, 2.3.8.4 and 2.3.8.6 we have

$$h = \Phi \text{Pr}^m \text{Gr}^n$$ \hspace{1cm} 2.3.8.7

$\Phi$, $m$ and $n$ can be found by experimental correlation for whatever system geometry and flow regime that are under investigation. In practice, $\text{Nu} = (\text{PrGr})^\theta$ where $\theta = \frac{1}{3}$ for laminar flow and $\theta = \frac{1}{2}$ for turbulent flow, is appropriate.

The Gr depends on $\Theta$ which itself depends on $\alpha$, the thermal diffusivity; since $\text{Pr} = \frac{H}{\rho \alpha}$, the criterion for determining whether the flow is laminar or turbulent should be $(\text{PrGr})$ for natural convection.

For $10^4 < (\text{PrGr}) < 10^9$, $\text{Nu} = 0.69(\text{PrGr})^{\frac{1}{2}}$

For $10^9 < (\text{PrGr}) < 10^{12}$, $\text{Nu} = 0.129(\text{PrGr})^{\frac{1}{3}}$

[McAdams 1957]
Experimental Work

The works described in this section were undertaken in three stages. Stage I involves investigation of high temperature fractography and its relation to microstructural evolution. It can be noted that parts of this work was undertaken previously as referenced in section 1.041 of this thesis.

Stage II involves experimental determination of solute element segregation. The thin foil discs made from materials on which heat treatment I was applied were used in the segregation analysis in Stage II. The historical background of heat treatment I is from Kernforschungzentrum, Karlsruhe, FRG.

In Stage III, heat treatment II was applied. High temperature mechanical behaviour and irradiation effects were investigated. Cooling rate determination was carried out on materials used in Stage III.

The main difference between heat treatment I and II is that in I, δ-ferrite was present but in II, it was removed by initial ageing for 2 hours at 970°C before austenitization, following recommendations by Wassilew and Dafferner (1986).

Material

The material (1.4914 and 1.4923 steels) was supplied in plate form by Kernforschungzentrum, Karlsruhe, FRG. Tensile/creep specimens were prepared to specification of 2.5mm diameter and 25mm gauge length.
Chemical composition of the material is given in table 1. KfK, also supplied additional heat treated and fractured samples with considerable treatment times.

3.1.2.0 Heat treatment

The heat treatment of ferritic stainless steel consists of austenitising and tempering. The higher temperature austenitizing treatment was conducted with the samples encapsulated in silica glass in an argon atmosphere. This glass was subsequently broken to expose the sample to the cooling medium. A platinum wound tube furnace was used for heating which was within \( \pm 3^\circ \) of the quoted temperature. Tempering treatments were conducted in air with an air cool. Where possible, each heat treated condition was given to two test specimens of stabilized alloy and to one of the unstabilized.

The following programme of heat treatments was applied. Prior austenite grain size was enlarged in the two cases by annealing for 2 hours at 1250°C and then austenitizing at 1075°C. Cooling rate from the austenitizing temperature was varied in order to induce a variation in the form of martensite.

In decreasing rates of cool, the cooling media adopted were water, oil, air and an interrupted quench comprising, aircool to 400°C, holding at this temperature for 24 hours before eventually cooled in air to room temperature.

All above conditions of heat treatment were investigated in the resulting martensitic state. In addition, samples of large austenite grain size (aircool) and normal austenite
grain size given air quenches were tempered for 30 minutes at 750°C. The effect of tempering was further investigated in the normal austenite grain sized, aircooled sample by reducing the temperature to 700°C and 650°C. Finally the effects of soaking at 590°C for 5084 hours and the effects of stress, through creep testing at a similar temperature and period of time, were investigated.

3.1.2.1 High Temperature Fractographic study

This was carried out on a Denison model T47E Creep and Stress rupture testing machine. The intention was to fracture each specimen at 600°C within 10 to 20 minutes of loading. The fracture induced was therefore ductile in nature and produced under similar relatively high rates of strain. Each specimen was smeared along its end threads with a copper-based anti-seize compound which was effective up to 850°C. It was then inserted carefully into the machine jaws and a thermocouple was wired into a position central to the specimen. An initial tension equivalent to 75 MPa stress was applied and the furnace was slid into position with its ends plugged to prevent heat losses. The specimen temperature was increased as fast as possible to 600°C (~25 minutes) and a five minutes stabilization period was allowed. Loading was started at a stress of 150 MPa and was increased by 37.5 MPa per minute until an extension was observable between loading on the machine scale (50:1). The load was then maintained to fracture except on a few occasions when a further load increment was added after 5 minutes to ensure fracture occurred within the required time. Upon fracture, the specimen was removed immediately to prevent excessive oxidation of the fracture surfaces.
Specimens were stored in small bottles in cotton wool and in the presence of silica gel. The elongation at fracture was measured with the aid of Venier calipers. This together with the stress to induce fracture and time to fracture are recorded.

3.1.2.2 Hardness Measurement
One end of the fractured specimen was removed, mounted in bakelite and ground to 1200 grade paper. Hardness value was then determined from the average of 5 readings recorded on a Vickers Pyramid Hardness Testing machine. It can be noted that a temper of approximately 20 minutes at 600°C must be added to the specimen heat treatment, since this was measured subsequent to fracture.

3.1.2.3 Optical Microscopy
The mounted specimens used for hardness testing were re-ground and polished to a fineness of 1 μm (diamond). These were etched in Vilella's reagent and studied under a Reichert MeF₂ optical microscope. Prior austenite grain sizes were determined in four relevant samples using intercept method. A number of randomly chosen traverses were made totalling about 12 mm per specimen and the grain boundaries were identified at 640 x magnification. The following determinations were used.

Mean intercept grain diameter

\[
N_1 = \frac{\text{Total number of intercepts}}{\text{Total distance of traverse}}
\]
Grains per unit Vol. \( N_v = 0.422N_1^2 \)

Mean grain diameter from assuming a spherical grain ie

\[
V = \frac{4}{3} \pi r^3 = \frac{1}{N_v}
\]

The ASTM grain size was also determined.

3.1.2.4 Surface replica preparation

Surface replicas were prepared to reveal the nature of the fracture mode. One half of the fractured specimen was mounted in 'hard' bakelite so that the fracture surface was perpendicular to the surface to be polished. This was held in position with nichrome wire and a separate piece of the specimen was placed immediately in front of the fracture surface to prevent excess bevelling during polishing. The mounted specimen was then carefully ground to produce a section across the diameter of the fracture surface and polished to \( \frac{1}{2} \) micron grade (diamond paste). The specimen was etched in Vilella's reagent so that relief of martensite laths could be seen. A sheet of cellulose acetate was adhered to the specimen using a drop of acetone and removed when dry. The surface replica so formed was carbon coated and shadowed with gold. This carbon replica was transferred to a copper grid by slowly dissolving away the plastic backing in acetone.

3.1.2.5 Instrumentation

In this section, general description of applications and functional features of instruments used for various investigations in the present study are reviewed. The instruments used include the following:-
i) Scanning Electron Microscope (SEM)
ii) Transmission Electron Microscope (TEM)
iii) Scanning Transmission Electron Microscope (STEM)
iv) Field Emission Gun Scanning Transmission Electron Microscope (FEGSTEM)
v) Quantimet 800 Scanning and Image Analyser.

3.1.2.6 Scanning Electron Microscope (SEM)
This instrument is normally used to observe bulk specimens. It uses a fine electron probe (7-10 nm diameter) to illuminate the specimen. By scanning the probe across the specimen and detecting the low energy secondary or high energy primary backscattered electrons returning from the surface, an image may be formed. This returning electron signal is fed into a cathode ray tube (CRT) scanning at the same rate and a time dependent image is obtained (Williams, 1984).

Surface topography and/or elemental changes give rise to different signal intensities and hence contrast is obtained in the CRT. The SEM thus complements the internal imaging capability of TEM (Transmission Electron Microscope). Magnification is achieved simply by reducing the area of the scan raster and keeping the same display area. Secondary electron image resolution is limited by the probe size and therefore is generally in the range of 7-10nm [Fig. A.1.1]. This instrument can be used to examine fracture surfaces.
3.1.2.7 Dimple Size Analysis by SEM

Fracture surfaces were examined in a Cambridge Stereo scan 2A Scanning Electron Microscope at 30 kV accelerating voltage. The overall size and nature of the fracture surface was recorded by micrographs from a screen magnification of 100 x at both zero and 45° tilts. Micrographs for determining dimple sizes were taken at zero tilt at 2000 x magnification from central fracture regions i.e. away from the edges where roughly 45° angled shear surfaces were to be found.

Micrograph prints of fracture surfaces were produced at 1.5 times the SEM screen magnification. These were divided into either 9 or 16 sectors (according to dimple sizes) to make sizing easier. Each dimple was designated a size range by comparing it to a series of circles which differed in diameter by 2mm increments. These circles were in clear plastic so that they could be positioned on top of the dimple image. Data was collected, processed and stored on a BBC-B micro computer. Dimples containing a visible particle were distinguished from those without. A total of between 1000 and 3000 dimples were characterised for each specimen.

\( M_d \) represents the mean dimple radius and \( A_d \) represents the radius of a dimple with a mean area. In both cases, the shaded columns indicate dimples with a visible particle.

3.1.2.8 Transmission Electron Microscope (TEM)

This instrument uses a static beam of 100kV electrons to illuminate a desired region (2-70μm diameter) of an electron transparent specimen which is immersed in the
objective lens of the microscope. The transmitted and forward scattered electrons are recombined by the objective lens to form a diffraction pattern in the back focal plane and a magnified image in the image plane. By using subsequent intermediate lenses, either the image or the diffraction pattern is projected onto a fluorescent screen for observation or a photographic surface for recording.

The microanalytical capability of the TEM was limited to the identification of phases using electron diffraction; but the advanced STEM has improved on this [Fig. A.1.2].

3.1.2.9 Scanning Transmission Electron Microscope (STEM)
The STEM combines the versatilities of the conventional SEM and that of the TEM. The union of TEM and SEM required three specific technical break-throughs. The creation of very fine probes of high kV electrons while maintaining the possibility of unrestricted large area scanning was necessary. This was achieved by the development of the condenser-objective lens system which uses the upper pole piece of the objective lens as a strong third condenser lens.

Beam scanning systems and detectors were developed within the confines of the TEM column, permitting the formation of time dependent scanning images while maintaining the capability of obtaining diffraction information in the back focal plane of the objective lens.

Signal detectors were developed to utilize all the useful information generated in the specimen [Fig. A.1.3].
This instrument is capable of complete analysis of a material in terms of microstructure, crystallography, degree of crystallinity and through-thickness chemical composition.

A further development to the STEM is the combination of a Link System for elemental microanalysis (STEMMA). The STEMMA has all the capabilities of TEM and SEM to define microstructure quantitatively as well as to perform simultaneously the structural and chemical analysis of portions of the specimen on a scale of tens of nanometers.

The major improvements on the STEM as compared to SEM include (i) large spatial resolution due to finer probe size (1-2nm) and high accelerating voltage, (ii) application extended to thin films in which minimum absorption or fluorescence correction is applied to x-ray data. The SEM can only handle bulk specimens while the STEM can be used for special application on thin films. The advanced STEMMA show further improvement in that microanalysis of elemental composition in materials are possible. Analysis from the STEM/STEMMA produce more qualitative results than that from the SEM. More information is obtained about samples from STEM/STEMMA analysis than from the SEM due to minimum speed of the focused electron beam. Profiling techniques on thin films are possible on the STEM/STEMMA allowing analysis up to 20 nm depth from specimen surface; whereas in the SEM, only the surface analysis is possible.

However, the presence of spurious x-rays generated in the electron column, specimen holder, and x-ray collimator are problems, yet to be attended in the STEM. These x-rays can make their way in one form or another into the EDS detector. Further, the small currents in the electron beam combined with the small excitation volume in the thin foil,
lead to low x-ray count rates. These low count rates limit the detection of small amounts of elements in a specimen as well as the accuracy and precision of an analysis.

Contamination layers may build up on the surfaces of thin foils and cause analytical error.

3.1.3.0 Energy Dispersive X-ray Analysis (EDX)
The EDX is based on the principle that energies of x-rays are characteristic of elements generating them. Detailed theory of energy dispersive x-ray analysis can be obtained from the literature [Hren, Goldstein and Joy (1979), Scott and Love (1983), Lorimer (1977) and Beaman (1978)].

When high energy electrons from STEM incident beam impinge upon elements in specimen, they excite them. When these elements return to their ground state, they emit x-rays with characteristic wavelength and energy. These x-ray energies are analysed by a solid state silicon wafer drifted with lithium in the EDS. Greater proportion of these x-rays can reach the detector held at 20°C above the horizontal plane by tilting the specimen in STEM, 30-45° to the horizontal. The EDS detector has a resolution of about 180eV (full width half maximum). This resolution allow distinction among the $K_{\alpha_1}$ x-rays generated by chromium ($Z=24; K_{\alpha} = 5.411$), Iron ($Z=26, K_{\alpha} = 6.398$) and nickel ($Z=28, K_{\alpha} = 7.474$).

Peaks produced by $K_{\beta}$ x-rays can superimpose on $K_{\alpha}$ peaks of the element with one higher atomic number. This problem can be overcome by either computer processing or manual deconvolution of EDX spectra.
Beryllium windows (6 μm thick) are usually incorporated as interface between STEM and EDS detectors to absorb low-energy x-rays. Since the detector efficiency is limited by low-energy x-rays; only x-rays to energies greater than 1.2 KeV can achieve useful results. This is the basis of analytical restriction of the EDS to elements with atomic number greater than 11 or 12.

After obtaining x-ray spectra, each spectrum was processed using Link Computer Program 860 RTS 2/FLS (Ratio Thin Section 2/Fit Least Squares) and its subroutines to obtain respective elemental composition on lath boundaries.

Firstly, tantalum spectra are used for calibration of the EDS and cobalt peaks were used as standard to sample peaks. The $K_a$ peak areas of the compositional elements were measured and their compositions worked out.

Corrections were made for atomic number, $K_B$ and escape peaks, but not for absorption, fluorescence or specimen thickness.

Concentrations of silicon, molybdenum, nickel, vanadium on lath and lath packet boundaries were obtained.

3.1.3.1 Analysis by STEMMA

Transmission Electron microscopy was undertaken on a JEOL-JEM-100CX Scanning Transmission Electron Microscope with Link System 860; characteristic x-ray data processor for elemental microanalysis.

Among procedures required in order to obtain appropriate operation conditions for the JEM-100CX electron microscope are:
1) Illumination system alignment
2) Objective lens current centering
3) Objective lens voltage centering
4) Objective aperture alignment
5) Objective Astigmatism correction

Further details about these operations are available in the manufacturer's manual.

The 100KV electron beam is focused to <10nm diameter at the thin foil specimen surface. Scanning coils move the focused beam over the specimen to obtain a STEM image. Quantitative electron probe microanalysis can be achieved when the focused beam is positioned at selected points on specimen surface.

In this present study, two techniques were used;
(i) Thin foil and (ii) extraction replica techniques.

3.1.3.2 Preparation of thin foils
From the gauge length portion near the fracture surface, discs were spark cut and punched to 3mm diameter discs using a die. These 3mm discs were ground to 100µm using varied sets of abrasive papers. The 100µm thick discs were thinned using 10% perchloric acid in ethanol at sub-zero temperatures in a Metal Thin Electropolishing rig. The perforated thin foils were then stored for analysis on the STEM.

3.1.3.3 Preparation of extraction replica
Carbon extraction replicas were prepared by etching the specimens mounted for optical examination in 10% HCl in
methanol. The etched surface was film coated by carbon and 1mm squares were marked on the carbon film surface before etching again. The 1mm squares of film were stripped in 10% HNO₃ and 2% HCl in methanol. The stripped 1mm square films were washed in methanol before they were lifted on copper grids and stored for the STEM analysis.

3.1.3.4 Characterisation of secondary carbide particles
The versatility of the STEM linked with EDX Link 860 was utilized in the determination of particle type and morphology. Elemental microanalysis of particles was possible by the detection of characteristic x-rays generated on probing a particle in the STEM mode.

3.1.3.5 Quantimet 800 Image Analyser
This instrument operates on the basis of a video scan of any wanted region in a field. Detection of a particular feature can be achieved in terms of whether the feature is lighter or darker than a chosen threshold level or between two such levels. These levels may lie anywhere between black and white and can be set either manually or automatically. The detector receives the video signal from the scanner via system control. Inside the detector, the video signal is compared with two reference levels set by the computer. These reference levels are known as thresholds A and B. In normal operation, a detected output is produced when the video level is between these reference levels.

The required degree of accuracy of measurements will influence the choice of detector. The detector has to
overcome imperfection in the video signals fed to it. Since the scanning beam is of finite size, the leading and trailing edges of the video signal produced when the feature is scanned also have finite duration and therefore sloping edges [Fig. A.1.5]. Other factors such as imperfect specimen focus, finite optical resolution and deficiencies in specimen preparation can contribute further to the degradation of the video signal.

The detected video signals representing the chords of detected features are fed to the standard Analyser MS3. From these signals, the MS3 computes parameters such as area, intercept and perimeter. A feature is correctly detected when the threshold level is such that the edges of the feature intercept the scan line at their half-contrast points [Fig. A.1.6].

3.1.3.6 Quantitative and Qualitative Analysis of carbide particles
These were done by using a Cambridge Quantimet 800 Scanner and image analyser. Microstructural parameters such as volume fraction, particle size, interparticle spacing and particle size distribution were determined through computer assisted video scanning and detection system incorporated in the equipment.

Among important steps to take before equipment is ready for use are

i) Putting the equipment on and allowing it to warm up for about one hour.

ii) Calibration of the image analyser.
iii) Setting of shading correction

iv) Setting of detection levels

There are two options in the module of the detection system; the basic field measurement and feature measurement options. About 1000 particles overall were investigated per each heat treatment condition. For the determination of particle size, measurement by equivalent diameter was selected in the feature mode while for the determination of volume fraction and inter-particle spacing, the field option was selected. Statistical data of carbide particles were obtained for aircooled tempered and untempered specimens.

The volume fraction calculation was done by expressing area occupied by the particles as a fraction of total area scanned by the detection system. The interparticle spacing was obtained by subtracting the obtained mean particle diameter from the obtained mean centre to centre distance between two particles. Details of this calculation can be found in operation manuals.

3.1.3.7 Carbide particle size analysis
Carbon extraction replica were analysed using STEM and Quantimet 800. Carbon extraction replica micrograph prints were used to establish the particle size and distribution within the alloy at the time of fracture. Enough micrographs were recorded to display about 500 particles in total. Prints were made at twice the magnification of micrograph negatives. The size and distribution of particles was conducted on a Quantimet 800 machine at the features mode.
3.2.0.0 Modelling of Solute Segregation

Fortran programs entitled 'Segne. fortran and 'Segage. fortran were provided by R.G. Faulkner for the determination of solute segregation via a combined equilibrium and non-equilibrium process in ferritic/martensitic steel (DIN 1.4914). Alloy solute elements constants were either calculated using techniques previously reported [Faulkner 1981, 1985, 1986] or obtained from the literature.

The lists of constants for respective solutes in the alloy were filed and used as data base for running the segregation programs [Appendix 3; 2.1 and 2.2].

Parameters such as tempering or ageing temperature were varied to examine effects on extent of segregation.

3.2.1.0 Field Emission Gun Scanning Transmission Electron Microscope (FEGSTEM)

The development of field emission gun (FEG) as an alternative electron source by Crewe and co-workers (1971) has enabled useful beam current (lnA) to be achieved in probes of sizes in the 1nm range.

Suitable demagnification, through one or more lenses of the apparent source crossover in the gun can be applied to obtain the required probe diameter. When the lenses produce a perfect image of the source, then the current in the probe can be given by

\[ i = \pi^2 B \alpha^2 d^2 / 4 \]

where \( B \), \( \alpha \) and \( d \) are respectively the source brightness, the convergence semi-angle and the diameter of the probe.
The probe diameter is usually defined as that which contains a given proportion of the total current, usually 80% or 90%. The probe is aberrated by diffraction, spherical aberration and chromatic aberration (plus astigmatism and other aberrations). Spherical aberration normally limits the maximum value of $\alpha$ which can be used. According to Crewe (1971), for a required minimum current and spatial resolution, the brightness $B$ must exceed the value derived from theoretical calculation.

The value of $B$ for the cold field-emission cathode operating at 100kV accelerating voltage is typically $10^7$ Amm$^{-2}$ Sr$^{-1}$. This is an improvement in the FEGSTEM as compared to the STEM with $B$ value of $5 \times 10^4$ Amm$^{-2}$ Sr$^{-1}$ for an LaB$_6$ source. Also one thousand times more energy can be put on the FEGSTEM to generate more x-rays than possible in the STEM.

As the convergence angle of the probe is reduced, it is possible for the probe to be limited by diffraction. The diffraction diameter can be expressed as $d_\lambda = \lambda / \alpha$, where $\lambda$ is the electron wavelength. A similar 'diameter' can be defined for spherical aberration as

$$d_s = C_s \alpha^{3/2}$$

where $C_s$ is the spherical aberration coefficient.

Thomas (1982) and Munro (1977) made more accurate estimates of probe diameter using wave optics calculations requiring numerical integration by computer for FEGSTEM system with similar electron optics to that in HB501. Their calculations showed that a minimum probe size of diameter <1nm, containing 80% of the incident probe current, is possible.
Titchmarsh et al (1987) presented an excellent description of this system installed in Harwell Laboratory (HB501 FEGSTEM). The field emission electron source is an oriented tungsten single crystal with a \( <310 > \) zone axis parallel to the optic axis. The crystal tip is etched to a fine point and positioned close to the first anode of the gun, which is held 3-4kV positive from the tip [Fig. A.1.3.1]. The intense electric field at the tip allows electrons to escape by tunnelling through the potential barrier at the crystal surface. A second anode accelerates the electrons to 100 KeV energy. Stable electron current emission requires a gun vacuum \(<10^{-10}\) torr.

Focusing of the beam can be obtained with the 'gun lens'. Adjustment of gun lens strength allows formation of an image \( S1 \) close to the differential pumping apertures which maintains a pressure differential typically \( x10^2 - x10^3 \) between the gun chamber and the rest of the microscope.

By using two condenser lenses, \( C1 \) and \( C2 \), images of the source can be transferred to the plane, \( S3 \), of the selected area diffraction aperture (SADA).

Varying the excitation of \( C1 \), caused the position of the intermediate crossover, \( S2 \), to change so that the strength of \( C2 \) can also be varied to maintain a fixed position for \( S3 \).

These variations, however, affect the demagnification of the source and the convergence angle, \( \alpha \), at \( S3 \). Hence, \( C1 \) and \( C2 \) in combination can be used to adjust size of probe, \( S4 \), at the specimen, together with the convergence angle, \( \alpha \) [Figs. A.2.3 and A.2.4].

The value of \( \alpha \) is determined by the aperture which is the field-limiting aperture of the system eg. objective aperture (OA) or virtual objective aperture (VOA).
For imaging, diffraction and energy loss analysis (EELS) the OA is normally used while the VOA with a small SADA is used for energy dispersive X-ray analysis (EDX).

If an OA is inserted, an additional spurious X-ray signal is always detected which reduces the validity of results. The VOA is optically conjugate, approximately, with the OA, and so its use does not prevent imaging. The physical size of the VOA is much smaller than the OA required to produce the same value of \( \alpha \), and the smallest VOA used to date (25\( \mu \)m diameter) limits the probe diameter for EDX to 2nm.

The X-ray detector is a 30mm\(^2\), "windowless" crystal which can detect characteristic X-rays from elements with atomic number 5 or above. The analysing system is the Link systems AN 10000, which is also interfaced to EELS 80/501 for acquisition and storage of EELS spectra. EELS spectrum resolution is better than 0.75eV on the zero energy loss peak. The AN1000 computer can also be used for digital scanning of the electron probe and the acquisition of X-ray elemental maps.

Imaging in STEM is related to imaging in conventional TEM by the principle of reciprocity (Pogany et al 1968). If the probe convergence angle in STEM is similar to the objective aperture in the TEM and the collector aperture in STEM is the same as the TEM illumination angle, then the images of same object in a STEM and a TEM will be identical. However, these two types of imaging are rarely performed in practice, with these equivalent aperture angles. The STEM collector angle is often much larger than typical TEM illumination angle, with the result that diffraction contrast effects are reduced.
The FEGSTEM offers an accurate method for studying solute element segregation. The high resolution imaging in FEGSTEM ensures that particle-free boundaries can be selected for analysis.

The larger $S$ value of the FEGSTEM gives very much larger current to produce better X-ray detection compared to the conventional STEM.

The finer probe in the FEGSTEM enabled very narrow compositional changes close to boundaries to be investigated compared to the conventional TEM/STEM which allowed analysis to a relatively coarse scale.

Table 2.9 shows characteristics of FEGSTEM (HB501) compared to STEM (JEOL-100Cx).

3.2.1.1 Experimental Determination of Solute Segregation

Thin foils were examined in a VG HB501 Field Emission Gun Scanning Transmission Electron Microscope at the Harwell Laboratory, to obtain both high resolution imaging and high spatial resolution data on chemical composition. [Titchmarsh et al 1987].

Thin foils were also examined in a JEM-JEOL-100Cx conventional Scanning and Transmission Electron Microscope at Loughborough University.

Microstructural examination was first carried out in order to select precipitate-free martensitic lath boundaries for subsequent chemical analysis.
Segregation profiles were then constructed by taking x-ray counts from a series of point analyses at distance of 5-200nm from the lath boundary, with the latter, oriented with its plane parallel to the electron beam direction.

A total of 300-400 lath boundaries were analysed for each cooling rate condition using both FEGSTEM (HB501) and STEM (JEOL-100Cx) facilities.

Majority of the analyses were carried out on the JEOL-100Cx being more readily available than the FEGSTEM. 30-50 lath boundaries were examined on FEGSTEM, while 300-350 lath boundaries were examined on STEM (JEOL-100 Cx). Mean segregation profiles were constructed from those lath boundaries exhibiting significant segregation.

3.2.1.2 Analytical Instrument Efficiency Determination

In a selected thin foil specimen, from a water quenched sample, labelled precipitate free lath boundaries were analysed using the FEGSTEM (HB501) and the conventional STEM (JEOL-100Cx).

Mean segregation profiles were constructed using data obtained from each instrument. Five particular lath boundaries were marked and analysed in both instruments to obtain a specific data trend. Segregation profiles were also constructed for these boundaries.
3.3.0.0  Materials/tensile specimen preparation

Large plate of DIN 1.4914 steel was obtained from KfK Karlsruhe.

Offcuts were processed, at Harwell, to 1mm thickness and tensile specimens to Harwell specification (AH 393/4759) were die punched from material bulk. Investigations required include effects of cooling rate, tempering temperature, test temperature and irradiation on high temperature mechanical behaviour. Hence, 54 specimens were retained as controls and the rest were reserved for irradiation. Control specimens were arranged in three groups of 18. This enabled three variations for cooling rate, tempering temperature, test temperature and allowed allocation of two samples per test temperature.

3.3.1.0  Heat treatment II

Heat treatments of 108 tensile specimens, from 1.4914 steel, were carried out in an inert atmosphere in a vertical tube furnace adapted to permit variations in cooling rates. An improvement over the heat treatment set up in section 3.1.2.0 was a designed vertical tube furnace with incorporated inert gas inlet seals. Heat losses due to time lag in breaking silica glass were avoided and heat hazards were minimised in this case.

Samples were heat treated at 970°C for 2 hours to remove traces of ß-ferrite phase, [Wassilew and Dafferner (1986)] then austenitized at 1080°C, with furnace tolerance of ±2°C, for 30 minutes before quenching in air, oil and water. A set of samples were tempered at temperature range 650-750°C in steps of 50°C.
3.3.2.0 Quenching rate determination by experiment

3.3.3.1 Sample preparation/procedure

[Fig. 3.48] The tensile specimen (1.4914 steel) was soaked in Analar grade methanol for about 30 minutes. Absorbent rag was used to clean its surface. A K-type thermocouple (N Cr-AlN) was arc welded to the middle part of the gauge length of the specimen using weld metal of about 1000°C melting point. A chromium wire was used to hang the specimen vertically in the furnace. The thermocouple leads were attached to a Nicolet brand digital analogue oscilloscope with four memory channels. A digital multimeter was connected to show voltage dropping as quenching progressed. The oscilloscope was connected to an output device (chart recorder) from which plots of voltage against time were later obtained. The furnace temperature was increased gradually until it reached the solution treatment temperature (1080°C). The specimen temperature recorded by the attached thermocouple was 620°C. The specimen remained at this temperature for 30 minutes. Meanwhile the oscilloscope was set at 200mS per signal point and 100mV voltage range. The chart recorder speed was at one second per centimeter and voltage range 0-4V for 40 times amplification of plots.

At the end of 30 minutes, the oscilloscope trigger was engaged at the same time the specimen was dropped directly into a bowl filled with quenching medium. It was essential that one ensured synchronisation between time of specimen immediate contact with quenching medium and the push of the oscilloscope trigger. Cooling curves were obtained for quenching in air, oil and water.

Experiments were repeated four times for each medium. Mean quenching rate data were calculated.
3.3.2.1 Obtaining Cooling rate from experimental curves
A straight line was constructed from the point when the cooling rate began to the point when the specimen was at room temperature. This line is taken as the slope of the cooling curve and its value was computed. These slope values obtained for respective cooling media were converted from the thermocouple (millivolt/sec.) to degrees C per sec using international standard table for K-type thermocouples.

3.3.3.0 High temperature tensile test of unirradiated samples
After heat treatment II of tensile specimens; they were soaked in methanol to remove dirt residues from the cooling media. On the flat edge of each specimen, labels were engraved to reflect the quenching medium, the tempering temperature and to show whether the specimen is unirradiated or irradiated. Labels number 1-6 are associated with unirradiated specimens, while 7-12 are for the irradiated. Label letters A, B, C are associated with 650°, 700°, 750°C tempering temperatures respectively. For example, a specimen labelled AAI can be identified as an aircooled, tempered at 650°C and unirradiated while that labelled OC7 can be identified as an oil quenched; 750°C tempered and irradiated specimen.

These formulations were adopted to enhance ease of identification at any stage of investigation; especially when tests are carried out in remote control cells.

The M3000S Universal Tester was employed in this investigation. This is a machine designed to test instruments in tension and compression. Its maximum force capacity is 20kN. Its load measuring system consists of oscillator demodulator electronics and incorporates a reference voltage generator to achieve electronic calibration.
Details of operational procedures are available in the manufacturer's manual. On getting the machine ready for operation, each specimen was bolted at both ends very tightly and inserted carefully into the machine jaws. A thermocouple was wired to a position central to the specimen gauge length to monitor the temperature at that point on the specimen. Two other thermocouples were wired to the top and bottom of the jaw respectively to monitor uniform thermal distribution in the furnace. A pre-stress level of about 1 MPa was allowed for each specimen to obtain fairly tight set up.

The furnace was then slid into position with its ends plugged to prevent heat losses. The specimens were allowed 15-20 minutes incubation time at a preset testing temperature before straining began.

The operating strain rate was $1.57 \times 10^{-4} \text{s}^{-1}$ when crosshead speed setting was at 0.2 mm per minute and at maximum operating load of 2 kN.

The progress of straining was observed on the computer screen until fracture occurred. As the specimen fractured the machine was stopped and parameters such as displacement and time to fracture were recorded. Using the computer, the stress-strain curve was analysed and mechanical strength data were obtained. These tests were carried out at temperatures 500, 600 and 650°C for each set of samples (2 per set), in order to obtain high temperature data trend.

3.3.3.1 Microstructural Analysis

From materials on which head treatment II was applied, thin foils were prepared by obtaining 3 mm discs at regions close to the fracture area using a die punch. The discs were then thinned using standard techniques described in the earlier sections to suitable perforation appropriate for transmission electron microscopy.
Carbon extraction replicas were also prepared from fractured and unfractured specimens.

Both thin foils and carbon extraction replicas were investigated using scanning transmission electron microscope.

3.3.3.2 Carbide particle analysis
Carbon extraction replica micrographs were obtained which display ≈500 particles per each heat treatment condition in total. Prints were made at twice the magnification of micro-STEM negatives. These particle images were analysed on Quantimet 800 and parameters such as particle size, distribution, volume fraction and interparticle spacing were determined.

3.3.3.3 Hardness Measurement
Vickers hardness was determined on tensile specimens upon which heat treatment II was previously applied.

Hardness values were obtained at room temperature for the unaged samples and at 650°C for the aged ones using 10Kg load.

Mean hardness values were obtained by taking average of 3 readings recorded on a Vickers Pyramid Hardness Testing machine.
3.3.4.0 Irradiation Procedures

Materials irradiated were those upon which heat treatment II was applied. Neutron irradiations of tensile specimens, of the geometry described previously, were carried out in the PLUTO nuclear research reactor at Harwell. A type 850 Rig located in a B6 hollow fuel element position was used. The irradiation was carried out at a controlled and measured temperature of 650°C ± 3°C for irradiation period of one reactor cycle. This corresponds to 525 hours at an average reactor power of 25.5MW. The calculated neutron spectra for this irradiation facility have been previously reported [Harries et al, 1962].

The irradiation rig comprises three carriers arranged vertically and spanning the reactor core centreline. Each carrier houses three specimen cartridges, with each holding six tensile specimens. A total load of nine specimen cartridges containing 54 tensile specimens were irradiated. Specimens were divided into nine heat treatment II conditions, thereby allowing six specimens per heat treatment located in an individual specimen cartridge. Specimens were interleaved with molybdenum foil to provide good thermal contact and to prevent specimen adhesion.

Control specimens to distinguish between irradiation effects and thermal ageing effects were thermal aged at 650°C for 525 hours.

3.3.4.1 Irradiation Dosimetry

Nickel and Cobalt flux monitors were incorporated in all three carriers, and used to determine the integrated thermal and fission neutron doses respectively, following standard
standard procedures [Harries et al, (1962) and (1964)].

The cross sections and half-lives used in calculating the results are tabulated; whence the results for the nickel monitors were corrected to allow for the burn up of Co\textsuperscript{58m} and Co\textsuperscript{58} by thermal neutrons.

The thermal neutron dose is constant down the rig at $3.478 \times 10^{20} \text{n.cm}^{-2}$, whereas, there is a small axial spread in fission neutron dose, covering the range $1.011 - 1.231 \times 10^{20} \text{n.cm}^{-2}$.

Fission neutron doses may be converted into the conventionally quoted doses with energy $\geq 1\text{MeV}$, through the following conversion.

Dose, $E>1\text{MeV} = \text{Fission dose} \times 0.795$. \hspace{1cm} 3.3.1

The conversion factor has been derived for the PLUTO nuclear research reactor from multi-foil spectrum analysis [McElroy, (1983)].

It is also of interest to convert fission doses into displacement damage dose units ($\text{dpa} = \text{displacement per atom}$).

The conversion, for the Harwell nuclear reactors calculated, using the RECOIL CODE [C.A. English, (1985)] is as follows.

$$\text{Damage, dpa(Fe, NRT)} = (\text{dose, } E>1\text{MeV}) \times (\text{damage parameter, } E>1\text{MeV})$$

$$= (\text{fission dose} \times 0.795) \times (1.919 \times 10^{-21})$$

$$= (\text{fission dose} \times 1.526 \times 10^{-21}$$

where dpa units are in the Norgett-Robinson-Torrens (NRT) standard units (Norgett et al, 1972).
For top barrel: fission dose = 1.011 x 10^{20} n.cm^{-2}  
Displacement dose = 1.011 x 10^{20} x 1.526 x 10^{-21}  
= 0.154 dpa

For middle barrel: fission dose = 1.231 x 10^{20} n.cm^{-2}  
Displacement dose = 1.231 x 10^{20} x 1.526 x 10^{-21}  
= 0.188 dpa

For the bottom barrel: fission dose = 1.117 x 10^{20} n.cm^{-2}  
Displacement dose = 0.170 dpa.

3.3.4.2 Calculation of Helium generation during irradiation
For 1 reactor cycle at 650°C, Westcott fluence or thermal neutron flux = 3.478 x 10^{20} n.cm^{-2}.

The major component in 1.4914 steel that can generate helium in large quantity is Boron. Boron is comprised of two isotopes ie. \(^{10}\text{B}\) and \(^{11}\text{B}\).

Relative abundances for \(^{11}\text{B}\) and \(^{10}\text{B}\) are 80.2 at % and 19.8 at % respectively. Thermal cross section for boron is very large (~3836 barns) [C.K. Bullough, 1986].

Helium can be generated via \((n,\alpha)\) reaction as represented below
\[ ^{10}\text{B}(n,\alpha) ^{7}\text{Li} \] 3.3.2

Another component in 1.4914 steel that can generate helium is nickel, but not in large quantity.

Nickel can generate helium via two steps reactions.
\[ ^{58}\text{Ni}(n,\gamma)^{59}\text{Ni}(n,\gamma)^{60}\text{Ni}(n,\alpha) ^{56}\text{Fe} \] 3.3.3

[ Decay and Electron Capture; \(t_{1/2} = 8 \times 10^4\) years].
$^{59}$Ni can only be generated via $(n,\gamma)$ reaction from $^{58}$Ni. When $^{59}$Ni is produced, it can either decay with a half life of about 80,000 years or be transmuted by either $(n,\gamma)$ or $(n,\alpha)$ reactions to produce $^{60}$Ni and helium respectively.

Hence, the rate of helium generation from nickel is jointly governed by the rate of generation of $^{59}$Ni and the probability that further transmutation that may occur will be by $(n,\alpha)$ reaction.

However, previous work showed that helium generation via $^{58}$Ni$(n,\gamma)$ $^{59}$Ni$(n,\alpha)$ $^{56}$Fe at $3.5 \times 10^{20}$ n.cm$^{-2}$ Westcott flux is not significant i.e. (~0.011 appm) from 0.5 wt%Ni.

Since composition of nickel in 1.4914 is ~0.7 wt%; helium generation from nickel transmutation reactions will be negligible.

Boron content in 1.4914 steel is 70 ppm

Density of 1.4914 alloy = 7.833 g cm$^{-3}$

Av. Atomic wt ($\alpha$-Fe) = 55.8 g

$^{10}$B thermal cross section = 3837$^{\pm}$10 barns*  
$^{10}$B Av. atomic wt = 10.81

Obtaining helium concentration from $^{10}$B $(n,\alpha)$ $^7$Li we have

$$\frac{[\text{He}]}{N_{\text{alloy}}} = \frac{N_B^{10}}{N_{\text{alloy}}} (1 - e^{-\sigma \phi t})$$

$N$ = number of atoms  
$[\text{He}]$ = Helium concentration  
$\sigma$ = thermal cross section, $\phi t$ = fluence

$$\frac{[\text{He}]}{N_{\text{alloy}}} = \text{Concentration of helium in N. alloy atoms.}$$

*1 barn = $10^{-24}$ cm$^{-1}$
\[ \frac{N_{\text{He}}}{N_{\text{alloy}}} = \frac{55.8 \times 0.198 \times \text{wt}\%^{10}\text{B}}{10.81} \]
\[ = 1.022 \times 7 \times 10^{-5} \]
\[ [\text{He}] = 1.022 \times 7 \times 10^{-5} \left( 1 - \exp(-3837 \times 10^{-24} \times 3.478 \times 10^{20}) \right) \]
\[ = 1.022 \times 7 \times 10^{-5} \left( 1 - \exp(-1.334) \right)^* \]
\[ = 1.022 \times 7 \times 10^{-5} \times 0.737^* \]
\[ = 5.272 \times 10^{-5} \]

Hence, concentration of helium generated via $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction during one nuclear reactor cycle irradiation of 1.4914 steel is 52.7 appm.

*Fraction of remaining $^{10}\text{B}$ burnt up per cycle of PLUTO.

3.3.4.3 Tensile testing of irradiated specimens

The procedure is the same as previously described in section 3.3.3.0 except that the testing was carried out remotely in shielded cells.

3.3.4.4 Boron Autoradiography

Off cuts from heat treated 1.4914 steel on \( \approx 16\text{mm} \) diameter mounts were prepared using standard metallographic techniques (Hughes and Rogers, 1967). Cellulose acetobutyrate film was laid on the mounts and was allowed to dry. Both specimen and film were held in the reactor for few seconds to give a dose commensurate with the alloy boron content, and the track density of the film. The film was subsequently removed and etched in KOH for 30 minutes at 50°C to reveal the damage tracks caused by $\alpha$-particle or lithium ion. The metallographic sample was then etched with oxalic acid. Together with the
film, it was viewed, and photographed using twin optical microscopes. Transmission phase contrast microscopy was used to view the autoradiograph film.

3.3.4.5 Thin foil preparation of irradiated specimens
This was carried out using standard techniques previously described, except that all the steps were followed in shielded glove hoods to prevent exposure to radiation.

3.3.4.6 Dimple Analysis
SEM micrographs of fracture surfaces were obtained for both irradiated and unirradiated samples upon which heat treatment II was applied. Enough micrographs which show 300-500 dimples per heat treatment condition were obtained. Prints were made at 1.5 times the magnification of original micrograph negatives. The dimple images were analysed on the Quantimet 800 machine using both field and feature measurements mode. Perimeter and equivalent circle modules of the feature mode were applied to obtain dimple diameter, density and size distribution for both irradiated and unirradiated specimens.

Note: It is important to note that materials on which heat treatments I and II were applied fractured under different test conditions. For example in section 3.1.2.1 the tensile test was carried out on a creep and stress rupture machine for materials under heat treatment I, and in section 3.3.3.0 test was carried out on a machine designed for tension and compression tests for materials under heat treatment II. Hence, mechanical property data obtained from work in section 3.3.3.0 are more accurate than those obtained from that in section 3.1.2.1. Standard stress strain curves were obtained in section 3.3.3.0 (see Appendix 5).
4.0.0.0 Results

4.1.1.0 Thermally induced microstructure [Heat treatment 1]
Table 1.1 shows the chemical composition of the materials under investigation. Alloys were classified as (i) Quenched, (ii) Tempered (iii) Tempered and long term aged.

A softening effect of tempering was observed despite the fact that tempering and long term ageing at 600°C is known to induce secondary hardening. [Fig. 1.1]

The effect of cooling rate from the austenitising temperature and that of prior austenite grain on microhardness is not significant [Fig.1.2].

The heat treatment gave a quenched material microstructure dominated by a heavily dislocated martensite structure. [Fig. 1.3a]

Bundles of laths, ~0.5μm in thickness are observed as packets of about 50μm in diameter [1.3b, c, d].

Due to a short 600°C treatment during fracturing of the specimens, precipitates, predominantly M₂X needle-like phase were observed. M is mainly chromium and X is a combination of carbon and nitrogen [Fig. 1.4].

Small M₂₃C₆ and NbC particles were also observed on lath boundaries and on prior austenite grain boundaries. Fine L-iron carbide is also present [Fig. 1.5a].

In an oil quenched sample tempered at 750°C, traces of boundary migration can be seen. [Fig. 1.5b]
Tempering enabled carbon to come out of the solid solution causing reduced dislocation density [Fig. 1.5c] and micro-hardness values. Fig. 1.5d illustrates slip bands associated with dislocation tangles. Recrystallisation occurred to give a more spheroidal structure with copious carbide precipitation on all boundaries [Fig. 1.6a]. Fig. 1.6b illustrates formation of new sub grain as a result of tempering at 750°C. Fig. 1.6c shows reduced dislocation tangles as a result of higher temperature tempering. Fig. 1.6d and 1.6e illustrate effect of 750°C tempering on both stabilised and unstabilised alloy. The 650°C tempering produced a structure comparable to that of the quenched alloy [Fig. 1.7 a and b].

The $\text{M}_2\text{X}$ and $\Sigma$-iron carbide precipitates disappeared, and larger quantities of $\text{M}_{23}\text{C}_6$ and NbC were observed on lath, lath packet and prior-$\gamma$ grain boundaries after higher temperature tempering.

Large primary NbC, $\sim0.5\mu\text{m}$, are present in all specimens [Fig. 1.8].

Long term ageing effect at 590°C after tempering revealed additional phases (Fe$_2$Mo - Laves phase) on which further $\text{M}_{23}\text{C}_6$ was precipitated.

Fig. 1.9 shows a schematic isothermal precipitation curve for the various phases.

Table 1.3 shows variation in particle size and distribution for selected samples as a function of heat treatment.

The niobium carbide was observed and identified as a disc or rod shaped structures and the chromium carbides are platelike film or irregular structures. [Fig. 1.10].
Fig. 1.11 shows an isolated rod shaped structure analysed as niobium enriched particle of a size in the order of 15nm, in a tempered, oil quenched sample.

Fig. 1.12, also shows extraction replica micrograph of smooth face NbC and M_{23}C_{6} particles in oil quenched samples tempered at 650°C.

4.1.1 Dimple size data [Heat treatment]

The analysis of dimple size and the TEM replica revealed a classical cup and cone ductile features in all the fractured samples. Small and large dimple sizes were obtained [Fig. 1.13]. The distributions indicate a bimodal form in most of the samples. Larger dimples disappear as we go from quenched to tempered, to long term aged variations of heat treatment. Figs. 1.14 a-c show TEM micrographs of dimples with particles on fracture surfaces.

Dimples are accommodated within planes at 45° to the load direction indicating that fracture occurs on these planes [Fig. 1.14d]. The plot of dimple area mean radius and the reciprocal of the square root of interparticle spacing indicate a linear relationship [Fig. 1.16a].

4.1.1.2 Particle size data [Heat treatment]

Table 1.3 shows carbide particle data. Stabilised aircooled sample tempered at 750°C and solution treated (2hrs at 1250°C + 5 hrs at 1075°C) shows largest particle size while the untempered sample of similar solution treatment shows smallest carbide particle size. A relationship exists between fracture stress and the reciprocal of the square root of interparticle spacing [Fig. 1.15].
Fig. 1.16b shows relationship between volume fraction of carbide particles and tempering temperature. Carbide size distributions showed the effect of long term ageing [Fig. 1.17] and tempering temperature [Fig. 1.18 and 1.19].

4.1.2.0 Fracturing at 600°C [Heat treatment 1]
Fracture stresses are higher (450-550 MPa) and inter carbide particle spacings are smaller in the quenched than for the tempered samples (250-350 MPa). Elongation to fracture is higher in the tempered (25-40%) samples than in the quenched ones. [Table 1.2]

Fast cooling rate introduced larger dimples into the fracture surface. Smaller number of very large dimples can be observed for large prior austenite grain size compared to the normal grain size equivalent. There is also a marked reduction in dimples associated with particles [Fig. 1.21] in the unstabilised compared to the stabilised alloys.

Fracture surfaces of samples containing large prior austenite grain and those rapidly cooled show reduced number of large dimples due to tempering at 750°C for 30 minutes. However, the rapidly cooled martensite shows more larger dimples than those containing large prior austenite grain.

Dimple size distribution obtained for samples tempered at 650°C and 750°C for 30 minutes are similar, whereas the intermediate tempering (700°C) shows a distribution with more larger dimples.

Fig. 1.22 illustrates schematic picture of fracture surface morphology as a function of heat treatment.
Fig. 1.23 illustrates TEM micrograph of carbon replica from etched surface perpendicular to fracture surface in an oil quenched sample.

4.2.3.0 Solute Segregation Models [Heat treatment 1]

Figure 2.24 shows the effect of ageing temperature and time on silicon segregation. As ageing temperature increases, silicon segregation intensity decreases. As ageing time increases, silicon segregation gets to a peak and then decreases sharply.

Fig. 2.25 illustrates the effect of solution temperature, tempering temperature and cooling rate on the extent of silicon segregation. Fig. 2.26 shows molybdenum segregation as a function of ageing time, tempering temperature and cooling rate.

In Fig. 2.27, the relationship of molybdenum segregation, solution temperature, cooling rate and tempering temperature can be observed.

Fig. 2.28 and 2.29 show chromium segregation intensity as a function of solution temperature, cooling rate, tempering temperature and ageing time. In fig. 2.29a, aircooling produced peak chromium segregation at an earlier ageing time than was the case with either oil or water quenching. Chromium segregation appears to be present even after higher ageing temperature and faster cooling [Fig. 2.29] In figs. 2.30 and 2.31, boron segregation intensities are illustrated. Largest boron segregation intensity can be predicted at water quench range, and shorter ageing time. At higher ageing temperature, boron segregation diminished.
Figs. 2.32 and 2.33 show niobium segregation as a function of cooling rate, ageing time, and solution temperature. The water quench range shows peak niobium segregation at shorter ageing time compared to that at the oil quench range [Fig. 2.32]. In fig. 2.33, it can be observed that niobium segregation persists even at higher tempering temperatures.

Vanadium segregation intensity can be related to cooling rate, ageing time and solution temperature [Figs. 2.34 and 2.35a].

Figs. A2.1 and A2.2 illustrate the computer programme used in this investigation.

4.2.3.1 Experimental data [HB501 FEGSTEM] for Solute Segregation
[Heat treatment 1]
A high magnification FEG-STEM micrograph of a typical lath boundary which was subjected to microanalytical profiling and found to exhibit strong segregation is shown in figure 2.35b.

In all untempered specimens, silicon and molybdenum are the principal segregating elements [Figs. 2.36 and 2.37].

Nickel shows a generally high level of segregation overall [Fig. 2.36e]. Behaviour of nickel in this case is not yet clear since its level of segregation is far above its nominal composition in the material under investigation. Molybdenum and silicon segregation are detected on 17%, 38% and 75% of lath boundaries analysed for oil, water and air quenched conditions respectively. Remaining lath boundaries exhibit negligible segregation. [Table 2.7c]
Figs. 2.36 and 2.37 illustrate mean silicon and molybdenum segregation for the three cooling rates. In fig. 2.37 mean nickel and vanadium segregation seem to have their peaks at a later cooling rate range above that of water quench range.

These data [Figs. 2.36b and c) demonstrate that the oil quenched rate (50°C s⁻¹) is associated with maximum segregation of silicon and molybdenum [Table 2.7 a and b].

Tables 2.1 - 2.4 illustrate mean segregation data of profiles on lath boundaries for silicon, molybdenum and nickel segregation.

Figs. 2.36a and d show mean segregation profiles constructed near lath boundaries for silicon and molybdenum respectively. These profiles indicate that solute build up occurs principally within a region up to 10nm from the interface.

The effect of tempering on solute element segregation is illustrated in figs. 2.38 - 2.40. Molybdenum segregation seems to diminish after tempering at 650°C and 700°C, whereas at 750°C, it seems to segregate. This data is not yet clear. [Fig. 2.38].

Silicon segregation diminished considerably at all tempering temperatures [Fig. 2.39].

Nickel segregation seems to persist at all tempering temperatures. It is not well understood why nickel behaves in this manner. [Fig. 2.46].

Figs. 2.41 - 2.43 show evidence that the FEGSTEM (HB501) provides better analytical data compared to the conventional
STEM (JEOL-100CX). In fig. 2.44, sketch of beam spreadings on thin foil surface from FEGSTEM (HB501) and STEM are shown.

4.2.3.2 Solute Segregation related to mechanical behaviour

It can be noted that the segregation data obtained from materials upon which heat treatment 1 was applied and mechanical property data obtained from materials upon which heat treatment II was applied are considered. However, mechanical data and segregation data were obtained at similar test temperature (600°C).

Instrumented impact test data are presented in fig. 2.45. The fracture energy is a maximum for a cooling rate of 50°C/second, corresponding to peak silicon and molybdenum segregation, irrespective of tempering time or temperature. The effect is more pronounced for the 2hr/600°C and 2hr/750°C tempering conditions.

Fig. 2.46 illustrate the relationship between silicon and molybdenum segregation, and the total elongation at varied cooling rates.

Peak total elongation value was obtained at the oil quenched range coincident with silicon and molybdenum segregation peaks. The relationship of solute segregation, tensile yield strength and cooling rate is illustrated in fig. 2.47. Silicon and molybdenum segregation peaks are coincident with lowest yield strength. This is consistent, in that, reduced yield strength can be associated with increase in total elongation.
4.3.4.0 Quenching rate data

It can be noted that heat treatment II was applied to samples used for this investigation.

Fig. 3.48 shows the drawing of tensile specimen used for the quench rate experiment. Fig. 3.49 illustrates the block diagram of equipment layout for cooling rate investigation.

Calculations of slopes of cooling curves produce the cooling rates for air, oil, and water as 47, 115 and 345.5°C per second respectively. The cooling curves are illustrated in figs. 3.50 - 3.52.

Theoretical calculations of cooling rate, using McAdams equations for natural convection heat flow, produced cooling rate data for air, oil and water quenching conditions as - 53.4 - 327 and 8291.2K per second respectively. Fig. 3.53 shows the logarithmic relationship between the theoretical and experimental data obtained as linear, indicating some degree of accuracy in the experiment.

4.3.5.0 Tensile data for irradiated and unirradiated samples [Heat treatment II]

Mechanical property data were obtained for materials upon which heat treatment II was applied. It can be observed that increases in tempering temperature caused increases in total elongation and decreases in tensile yield strength [Table 3.18].

Irradiation at 650°C caused large increases in total elongation and large decreases in tensile yield strength in all samples [Table 3.19].

In fig. 3.54, carbide particle size is related to tensile yield strength. A peak yield strength can be observed at
a critical carbide particle diameter in unirradiated samples. Fig. 3.55a shows the effect of test temperature on carbide size distribution. Carbide size decreases with increasing cooling rate [Fig. 3.56]. Larger particle population was obtained for as treated water quenched than for the oil quenched samples [Fig. 3.57c].

The plot of tensile yield strength and carbide volume fraction is linear showing the carbide particle strengthening in aircooled samples tested at 600°C. [Fig. 3.58] It can be noted that the volume fraction data are for samples upon which heat treatment I was applied while the tensile yield data are for some samples upon which heat treatment II was applied. [Tables 1.3 and 3.18]

For the oil quenched samples, tensile yield strength relates linearly to the reciprocal of the square root of inter-particle spacing [Fig. 3.59].

An experimental drop of total elongation as volume fraction of carbide particles increases can be observed in figure 3.60. The total elongation data were obtained from samples upon which heat treatment II was applied while the volume fraction data were for similar samples upon which heat treatment I was applied.

Fig. 3.61 illustrates the specimen cartridge assembly used during irradiation. Generally, the fracture mode is ductile before and after irradiation. In fig. 3.62, a large inclusion on the fracture surface of an oil quenched sample tested at 500°C can be observed.

Fig. 3.63 and 3.64 show comparison between fracture surface dimples in a water quenched sample tempered at 750°C before
irradiation test at 500°C and after irradiation test at 600°C.

In figs. 3.65 and 3.66, the oil quenched sample tempered at 700°C and tested at 600°C shows reduction in the density of larger dimples after irradiation.

Figs. 3.67 and 3.68 illustrate necking during high temperature fracture of an oil quenched sample, tempered at 700°C and tested at 600°C before and after irradiation. Necking is more pronounced in the irradiated sample than the unirradiated.

Variation in fracture surface dimple dimensions can be observed as tempering temperature increases for an oil quenched sample tested at 500°C. [Figs. 3.69-3.71]. Larger dimple density is higher in the 650°C and 700°C tempering temperature than at 750°C.

Fewer large dimples can be observed in the irradiated, air cooled samples, tempered at 650°C and tested at 600°C, compared to the unirradiated sample. [Figs. 3.72 and 3.73].

Tearing processes can be observed on the side wall of water quenched and aircooled samples tested at 600°C before and after irradiation [Figs. 3.73-3.76].

4.3.5.1 Tensile Yield Strength
Tables 3.18 and 3.19 present the high temperature mechanical property data before and after irradiation respectively.
Figs. 3.77 and 3.78 illustrate the effect of test temperature on tensile yield strength with variations in cooling rate and tempering temperature.

No significant test temperature effects on yield strength can be observed for oil quenched samples tempered at 650°C and 750°C; and water quenched sample tempered at 700°C.

The test temperature effect on yield strength observed in an aircooled sample tempered at 650°C is not consistent with that obtained for the 700°C and 750°C tempering. This can also be observed in the case of oil and water quenched samples.

Tensile yield strength peaks can be observed at 600°C test for irradiated samples except for the 650 temper and aircooled; and the 750 temper and water quenched irradiated samples.

In figs. 3.79 and 3.80, the effects of cooling rate on high temperature tensile yield strength are illustrated. Test temperature and tempering temperature effects can also be observed before and after irradiation.

The largest yield strength was observed at the oil quench range for samples tempered at 650°C and tested at 500°C before irradiation.

After irradiation, largest yield strength was observed at the aircooling range for samples tempered at 650°C and tested at 650°C.

Tensile yield strength peaks were obtained before irradiation at the oil quench range for samples tempered at 650°C, 700°C, 700°C, 750°C and tested at 500°C, 600°C, 650°C and 600°C respectively.
The trend of cooling rate effect on yield strength is the same before and after irradiation for samples tempered at 750°C and tested at 650°C [Fig. 3.79c].

Figs. 3.81 and 3.82 illustrate the relationships of tensile yield strength, tempering temperature, cooling rate and test temperature before and after irradiation.

No significant effect of tempering temperature on yield strength in an irradiated, oil quenched samples tested at 600°C [Fig. 3.81b (ii)] can be observed.

Increases in yield strength with increasing tempering temperature can be observed in irradiated samples quenched in oil, water, air, and tested at 500°C, 500°C and 600°C respectively.

Oil and water quenched samples tested at 500°C; and air-cooled samples tested at 650°C show decreasing yield strength with increasing tempering temperature before irradiation.

Yield strength peaks at 700°C tempering can be observed for oil quench, and air cooled samples tested at 600°C and 650°C respectively before and after neutron irradiation. Dips of yield strength at 700°C tempering can be observed in water quenched samples tested at 600°C and 650°C irrespectively of irradiation.

4.3.5.2 Tensile Ductility

In Figs. 3.83 and 3.84, test temperature effects, tempering temperature effects and cooling rates effects on total elongation before and after irradiation are illustrated.
No significant test temperature effect can be observed in unirradiated, aircooled, water quenched and oil quenched samples tempered at 650°C, 700°C and 750°C respectively. Total elongation decreases with increasing test temperature for unirradiated aircooled and water quenched samples tempered at 700°C and 750°C respectively.

Total elongation peaks were obtained at 600°C test for irradiated samples tempered at 750°C irrespective of cooling rates variation.

For the unirradiated case; total elongation peaks can be observed at 600°C test in water quench, aircooled samples tempered at 650°C and 750°C respectively; whereas peaks were obtained at 600°C test for unirradiated oil quenched samples at all tempering temperatures. Ductility troughs are observed at 600°C test for irradiated aircooled and water quenched samples tempered at 700°C and 650°C respectively.

In Figs. 3.85 and 3.86; relationships of total elongation, tempering temperature, cooling rate and test temperature are illustrated.

At 700°C tempering, ductility dips were observed for oil-quenched samples tested at 500°C and 600°C irrespective of neutron irradiation.

Effects of tempering temperature on total elongation for water quenched samples tested at 650°C is quite minimum before and after neutron irradiation. A reduction in ductility can be observed after neutron irradiation for aircool, oil quenched and water quenched samples tested at 650°C, 650°C and 500°C respectively as tempering temperature increases.
Figs. 3.87 and 3.38 show effects of cooling rate test temperature, tempering temperature on total elongation before and after neutron irradiation.

Cooling rate effect on total elongation before neutron irradiation is smaller compared to that after irradiation in samples tempered at 650°C, 700°C and tested at 650°C.

Ductility peaks and dips can be observed before and after neutron irradiation respectively for 650°C tempered samples at the oil quench range for all test temperatures.

The effects of cooling rate on total elongation after neutron irradiation is prominent in 700°C and 750°C tempered samples tested at 600°C and 650°C.

Total elongation decreases with increasing cooling rate in irradiated, 650°C and 750°C tempered samples tested at 600°C and 500°C respectively.

4.3.6.0 Dimple size distribution for irradiated samples [Heat treatment II]
Irradiation has induced larger population of smaller dimples in an oil quenched sample tempered at 650°C and tested at 600°C [Fig. 3.89]. Few dimples are large in the irradiated case while there are significant number of large dimples in the unirradiated sample. In the irradiated water quenched sample tempered at 750°C, larger number of smaller dimples can be observed compared to the unirradiated case. The dimple size distribution indicate a bimodal form of both irradiated and unirradiated samples [Fig. 3.90].

It is interesting to know that irradiation induced larger dimple density in an oil quenched sample tempered at 700°C. [Fig. 3.91].
The distribution indicates more smaller dimples in the irradiated than the unirradiated case [Table 3.20].

Fig. 3.92 illustrates bimodal dimple size distribution in unirradiated, 750°C tempered samples as a function of cooling rate. The oil quenched sample shows more smaller dimples than at other cooling rates.

In the irradiated and unirradiated cases, a linear relationship can be proposed between fracture stress and the reciprocal of square root of dimple spacing [Fig. 3.93].

It is important to note that larger total elongation values obtained due to irradiation can be associated with larger dimple density [Fig. 3.94] and [Table 3.21].

A linear relationship exists between dimple density and total elongation in both irradiated and unirradiated cases.

In Fig. 3.95, the reduction in tensile yield strength induced by irradiation is related to the dimple density. It appears that the increases in dimple density show decreases in tensile yield strength. The unirradiated samples with larger tensile yield strength show smaller dimple density. [Table 3.22].

For the irradiated aircooled samples tested at 600°C, largest dimple size was obtained at 700°C tempering [Fig. 3.96]. This data was supported by Fig. 3.94 indicating smallest dimple density at 700°C tempering.

For the irradiated and unirradiated cases, the dimple diameter appears to relate with carbide particle diameter linearly. [Fig. 3.97]. There is an indication of a size cut off at about 0.06 microns. It is clearly observed that irradiation
caused reduction in dimple size, and hence the carbide particle size. [Tables 3.21 - 3.23]

It appears that a critical carbide particle size exists (~.005μm) below which particle assisted dimple formation is limited as illustrated in figs. 3.97 - 3.99 for both irradiated and unirradiated cases.

4.3.6.1 Ageing for 525 hours at 650°C

In Fig. 3.100, hardness minimum can be observed for the aged, air-cooled, unirradiated samples tempered at 700°C. For the air-cooled samples not aged, hardness increases with increasing tempering temperature.

Whereas in the oil quenched sample, the reverse can be observed. There is no significant effect of tempering on the hardness values of aged and oil quenched samples [Fig. 3.101]. In the water quenched sample aged at 650°C, the hardness value increases with tempering temperature whereas without ageing, no significant effect of tempering on hardness can be observed. [Fig. 3.102].

In the aged samples tempered at 650°C significant effect of cooling rate on hardness can be observed [Fig. 3.103] whereas in the unaged case, cooling rate effect on hardness is a peak at the oil quench range. Hardness decreases as cooling rate increases for the aged samples tempered at 650°C.

For aged samples tempered at 700°C, peak hardness can be observed at the oil quench range whereas for the unaged samples hardness minimum can be observed. It appears that effect of cooling rate on hardness is constant from the
oil quench range to faster cooling rates for the aged samples tempered at 700°C. [Fig. 3.104].

In fig. 3.105 significant effect of cooling rate on hardness can be observed for the unaged samples tempered at 750°C.

Tables 3.24 summarises the hardness data and illustrates proportionate contribution of thermal ageing effect and that of irradiation on the total elongation values obtained. In aircooled sample tempered at 700°C, oil quenched sample tempered at 750°C and water quenched sample tempered at 750°C, the larger contribution of thermal ageing effect on total elongation appear to be reversed by radiation hardning, In these samples radiation hardening effects superimpose on thermal ageing effects.

The average Youngs Modulus obtained from tensile test is 23679 MNm\(^{-2}\). This result compares very well with the literature value of 26500 MNm\(^{-2}\) (Cottrell, 1967) despite the fact that tension tests are known to be inappropriate for the estimation of Youngs Modulus. Table 3.25 and 3.26 show the fracture toughness data calculated from experimental data in table 3.19 and 3.18 respectively. Logarithmic plots of true stress against true strain provide slopes representing strain hardening exponents (n). These slope values were used to compute the crack opening displace­ment (\(a\)) and hence the fracture toughness (\(K_i\) and \(K_{IC}\)). Fig. 3.106 illustrate the relationship between critical fracture toughness (\(K_{IC}\)) and total elongation.
5.0.0.0 Discussions

5.1.1.0 Irradiation and thermally induced microstructure

The summary of microstructure observed due to heat treatment I and II is illustrated in Fig. 1.9. This is similar to that observed by Ehrlich (1986), Little et al. (1977) and Nutting (1983) for ferritic/martensitic steels.

In the quenched material, martensite forms at a relatively high temperature and consists of bundles of laths, with each sub-unit having a high and uniform dislocation density [Figs. 1.3a-d]. Large and undissolved primary niobium carbide particles are found randomly scattered throughout the microstructure [Figs. 1.10-1.12]. Low temperature temper at 650°C produces M$_2$X spread as needles throughout the microstructure [Fig. 1.4].

Inclusions such as manganese sulphide, alumina, silicates are known to be present in sizes as large as 5μm in diameter - [Figs. 1.22 and 1.23].

The fine precipitation observed in the quenched extraction replicas can be the result of slight tempering during the fracturing at 600°C [Fig. 1.5a].

The predominant second phase is the M$_{23}$C$_6$ which precipitated on lath and prior austenite grain boundaries [Fig. 1.7 and 1.8].

Tempering causes a relaxation of the highly dislocated structure via recrystallisation or recovery process [Figs. 1.6a-d].
At higher tempering temperatures, polygonisation and recrystallisation occur. [Figs. 1.5c and 1.6b-d]. The progressive increase in tempering temperature causes softening of the matrix [Figs. 1.1 and 1.6c]. The Nb stabilised steel shows appreciable tempering resistance due to its reluctance to recrystallise at higher temperatures and longer times [Fig. 1.1]. The explanation advanced for this phenomenon by Little et al (1977) showed a stabilising effect of Nb on the growth of M_{23}C_{6} which allowed unpinning of grain boundaries, only at higher temperatures, and the solute drag of Nb on boundaries during migration [Fig. 1.5b]. In the long term aged material, considerable coarsening of M_{23}C_{6} and replacement of the M_{2}X needles by MX(M = 37% V, 50% Cr) was observed due to secondary hardening. Formation of Laves (Fe_{2}Mo) phase can initiate, further precipitation of M_{23}C_{6}. These observations agree very well with that by Senior et al (1988) for 9Cr-1Mo steel. It is well known that M_{2}X and ε-iron carbides form during the quench [Fig. 1.5a].

There are existing evidences that irradiation can induce phase changes and precipitation in ferritic/martensitic steels. Detailed investigations on irradiation induced phase changes are not included in this present study.

However, previous reports by Gelles (1983), Little et al (1982), Kayano et al (1985), Wassilew et al (1983), Klueh et al (1983) and Stamm et al (1987) showed evidence for irradiation-induced phases such as G-phase (nickel silicide), α', chi phases and large precipitation of M_{23}C_{6}. It is expected that similar phases can be observed in the present study. The presence of G-phase has been associated with irradiation induced solute segregation. Since irradiation in the present study is at 650°C, according to Hsu et al (1986),
no G-phase can be expected at such higher temperature. Hsu et al (1986) suggested that dissolution of G-phase occurs, above 500°C. The chromium rich $\alpha'$ phase is expected to be formed. Recovered dislocation and subgrain structures within the martensite laths are expected as cell structure characteristics of overtempered martensite. Gelles and Thomas (1982 and 1983) reported that no evidence of irradiation induced cavities was found in 12Cr-1MoVW steel irradiated at 400-550°C to fluence of 67 dpa ($E>0.1\text{MeV}$). At 84 dpa, cavities were found only in 12Cr-1Mo steel irradiated at 425°C, and no voids were found at higher temperatures. This observation is similar to that by Little et al (1982 and 1979) in their investigation of 12Cr-1Mo steel following irradiation to 23 dpa at 300-615°C. Among reasons advanced for the absence of voids include that by Wassilew et al (1983), that bubbles formed by helium gas produced by $(n,\alpha)$ reactions, are finer and well dispersed, hence, no bubble coalescence and growth can occur.

Vitek and Klueh (1983) reported that the increased amount of helium produced during HFIR irradiations enhanced the formation of cavities in HT-9 (12Cr-1Mo) in the temperature range 300-600°C, and a maximum cavity density observed at 400°C. The comparison by Gelles (1985) of microstructure of HT-9 (12Cr-1Mo) irradiated in HFIR to 39 dpa at 300-600°C to one irradiated in EBR-11 to 29 dpa at 390-500°C, showed that irradiation in HFIR promoted helium bubble formation at all temperatures and some cavity formation at 400°C, whereas no cavities were found in EBR-II irradiations. In this comparative study, material employed are of the same heat of HT-9, hence, swelling difference was attributed to helium generation via $(n,\alpha)$ reactions.
5.1.2.0 Fracture of irradiated and unirradiated specimens

5.1.2.1 Mechanical properties

In the present study, larger increases in total elongation and decreases in tensile yield strength were obtained for irradiated specimens compared to the unirradiated ones [Tables 3.18 and 3.19]. Clear evidence exists to show that the increases in total elongation and the decreases of tensile yield strength after irradiation can be attributed to the contributions by both thermal ageing and irradiation effects [Table 3.24]. The present results show that irradiation at 650°C contributed largely to the increases and decreases in total elongation and tensile yield strength respectively, compared to thermal ageing effect. Wassilew et al (1983) suggested that thermal ageing effect was largely responsible for increases in total elongations obtained in their investigation of same material. Hardness data obtained for material before and after ageing at 650°C for 525 hours (same as irradiation period) showed reductions not adequate to account for the increases in total elongation observed after irradiation at 650°C. Table 3.24 shows proportionate influences of both irradiation and thermal ageing effects on total elongation. The oil quenched alloy tempered at 650°C and tested at 500°C indicates highest thermal ageing effect on total elongation and tensile yield strength compared to that by irradiation while the water quenched alloy of same heat treatment shows highest irradiation influence on total elongation and tensile yield strength.

For example, in table 3.24 samples 2A, 7, 8 and 9 show larger thermal effects and hence, smaller irradiation effects; compared to samples 3A, 10 and 11 which show smaller thermal effects and large irradiation effects.

The reduced combined effects of thermal ageing and irradiation in samples 5, 9 and 12 show that thermal effect dominate
irradiation effect in those samples, but the observed smaller change in total elongation compared to other samples is surprising. It is possible that irradiation has caused an opposing effect to that of thermal ageing effect via some unknown mechanisms, probably, radiation hardening, to reduce the proportionate change in total elongation [Figs. 3.100 - 3.105].

5.1.2.2 Tensile yield strength
Irradiation and higher temperature tempering caused large reductions in tensile yield strength for all specimens. [Figs. 3.79 and 3.80]. These observations are similar to those of Schirra (1984), Maternal Morris et al (1987), Wassilew et al (1983), Klueh and Vitek (1983) and Stamm et al (1987).

Wassilew et al (1983) reported that reduction in tensile yield strength after irradiation at 590°C is independent of test temperature. In this present study, a test temperature dependence on yield strength reductions can be observed before and after irradiation. For example, for aircooled, irradiated samples tempered at 650°C and 750°C; and water quenched samples tempered at 750°C, the tensile yield strength decreases with increasing test temperature. However, increases in yield strength observed for aircooled, irradiated samples tempered at 700°C show that irradiation hardening effect rather than the test temperature independence is a possibility [Figs. 3.77 and 3.78]. It is interesting to note that peak tensile yield strengths are obtained at 600°C test for oil quenched, irradiated samples irrespective of tempering temperature. This is another evidence to support the combined effects of both thermal
ageing and irradiation on the microstructure. It is also possible that segregation of alloy impurities to grain boundaries play some role. According to McMahon et al (1979), segregation of metalloid impurities to grain boundaries can cause reductions of fracture toughness.

In the unirradiated samples, the effect of cooling rate on yield strength is pronounced. Peak yield strengths can be observed for the unirradiated, 650°C, 700°C, 700°C and 750°C tempered samples; and tested at 500°C, 600°C, 650°C and 600°C respectively. In the irradiated case, yield strength minima were observed at the oil quenched range for samples tempered at 700°C, 750°C and tested at 650°C and 500°C respectively [Figs. 3.79-3.80]. Explanation of these data is complicated. It is possible that other multiple effects other than cooling rate influence can be responsible.

5.1.2.3 Total Elongation

Irradiation and higher tempering temperature caused increases in total elongation in all samples. Test temperature dependence of total elongation is more pronounced in the irradiated cases than in the unirradiated cases. [Fig. 3.83 and 3.84]. This observation is due largely to irradiation induced recovery at 650°C and to some extent higher tempering temperatures causing softening of the matrix. Peak total elongations observed in irradiated samples tempered at 750°C and tested at 600°C irrespective of cooling rate variation show recovery effects independent of cooling rate.

According to Little et al (1982), radiation softening of the matrix and recovery effects can be rationalised in terms of observed decreases in network dislocation density [Fig. 1.6c].
These recovery processes can be associated with the rapid rates of dislocation climb induced by the high non-equilibrium concentrations of point defects generated during irradiation. For the irradiated, oil quenched sample tested at 600°C, no significant increase in total elongation can be observed [Fig. 3.85 and 3.86]. Also, for irradiated, air-cooled samples tested at 650°C and that of water quench tested at 500°C, total elongation decreases with increasing tempering temperature [Fig. 3.85 and 3.86]. From this observation, it appears that some multiple effects involving thermal ageing and irradiation hardening play some role. Calculations based on the Brown-Kelly-Mayer formulation indicated that the high binding energy between self-interstitials and nitrogen or carbon atoms (0.5eV) produces a marked reduction in the self-interstitial jump rate during irradiation, resulting in increasing density of interstitial clusters. [Little et al 1976]. This radiation hardening mechanism applies mostly at lower irradiation temperatures. However, it is not impossible that radiation hardening mechanism can be extended to higher temperatures, but for this present study, it will be surprising.

For irradiated and unirradiated samples cooling rate effects on total elongation is not pronounced. Peak total elongations were observed at the oil quench range for most of the samples before and after irradiation. [Tables 3.18 and 3.19]. This may be due to silicon and molybdenum segregation to lath boundaries which play some role in enhancing cohesive energy. Although, radiation-induced segregation of solute element has been associated with mechanical behaviour; nevertheless, radiation-induced segregation is unexpected for the short irradiation time and higher temperature employed in the present study. It is clear that radiation-induced phase changes will influence high temperature mechanical
properties of 12%Cr ferritic/martensitic steels. More work is required to provide evidence for this.

For the irradiated samples, it is possible that the presence of finely dispersed helium bubbles has influenced total elongation.

5.1.3.0 Fracture related to microstructure

The microstructure observed after varied heat treatment and irradiation of material under investigation suggests that the inclusion-matrix interface and the lath packet boundaries are the weakest. Figure 1.25 illustrates the origin of the deep dimple, based on an oxide or sulphide inclusion and the development of porosity behind the fracture surface and lath packet boundaries. It is more likely that carbide-matrix interface separation occurred largely in the vicinity of the lath packet boundaries or at particles on lath packet boundary intersections [Figs. 1.14d, 1.7 and 1.8]. The dimple size data showed bimodal distributions for the fast quenched and the long term aged or irradiated materials [Figs. 1.13, 3.89, 1.21]. The large dimples are clearly associated with alumina and manganese sulphide inclusions present in the material [Fig. 1.24]. The finer dimples can be associated with the fine carbide particles observed on lath and lath packet boundaries. An important observation is the disappearance of large dimples on fast cooling, higher temperature tempering, long term ageing [Fig. 1.14a-c, 3.87a-c]. Senior et al (1988) reported similar observation in their study of 9Cr-1Mo steel. Void nucleation are associated with the presence of inclusions and precipitates.
As tempering temperature and ageing time are increased, carbide size changes until reaching a critical value with a subsequent effect on the interparticle spacing. Senior et al (1988) showed that void spacing is the main determinant of fracture. It is clear from dimple size distribution that carbide particle spacing has influenced high temperature failure of ferritic-martensitic steel. Figures 1.15, 1.16b, 1.18 and 1.19 show support for this suggestion. A bimodal carbide size distribution observed in fig. 1.17 for the long term aged material is consistent with that of the dimple size distribution in figure 1.13. In figures 1.15 and 1.19, linear relationships exist for fracture stress, reciprocal of the square root of carbide spacing and tempering temperature. Higher tempering temperature induced large formation of finer carbides analysed as $M_23\text{C}_6$ and NbC. Fig. 1.16a showed linear relationships between dimple size and carbide particle spacing for the quenched (Q), tempered (T) and long term aged (A) or irradiated material.

Ashby (1966) related the stress required to open a crack ($\sigma_T$) at a precipitate-matrix interface to particle size ($d_{\text{crit}}$) and the strain applied at the interface ($\varepsilon$). This relation

$$\sigma_T = \frac{\alpha_f d_{\text{crit}}}{\ell}$$

where $\alpha$ is a constant, $\ell$ is a term involving the distance of dislocation loops from the particle during plastic deformation, applies, assuming no segregation effects occur on progressing through Q>T>A sequence [Fig. 1.16a]. In this case, the stress required for separation of the interface will remain constant. Since the strain produced at the interface by a fixed applied stress will be less for
harder matrices than for softer ones, the value of $\epsilon$ will increase on progressing through the $Q>T>A$ sequence. Hence, the critical particle size, above which particle-matrix separation can occur decreases with $Q>T>A$ sequence. Smaller particles were therefore, capable of producing dimples in the aged and irradiated materials than in the quenched; and for a given interparticle spacing, there would be a reduction in the mean fine dimple size [Faulkner et al, 1987]. These ideas agree quite well with those of Senior et al (1988). They showed that dimple volume fraction is related to plastic strain [Fig. 3.101]. Slow cooling, higher temperature tempering, irradiation and long term ageing effects caused disappearance of large dimples indicating some strengthening of the inclusion-matrix interfaces [Figs. 3.92; table 3.20]. Senior et al (1988) also showed that carbide-matrix interfacial strength decreases with increasing ageing time.

Among possible mechanisms by which this can occur are

(i) Impurity segregation to effective interfaces

(ii) Creation of hardness variations or quench-induced stresses at the inclusion-matrix interfaces eg. coherency strains. For ferritic/martensitic steels, Faulkner (1981) predicted that solute elements like silicon, boron, and phosphorus can segregate to effective interfaces via a non-equilibrium process at critical cooling rates of 20°C per second (silicon), 250°C per second (boron) and 50°C per second (phosphorus).

However, experimental evidences have been obtained in the present study which show that silicon and molybdenum segregated to lath boundaries largely at the oil quench range. [Faulkner et al (1987)] [Figs. 2.36 and 2.37]. Since non-equilibrium segregation disappeared in slow cooled, tempered or aged samples, it is possible that boron, silicon,
phosphorus and molybdenum segregation can influence the initiation of large dimples. It is also possible that segregation of these elements promote stronger inclusion-matrix interfaces. This idea cannot be substantiated, since, evidence from the present study show that higher tempering temperature and long term ageing promoted desegregation of impurities to interfaces [Fig. 2.45]. According to McMahon and Vitek (1979), metalloid impurities segregation to interfaces can influence fracture toughness.

It can be expected that coherency of large inclusion size with the matrix will be smaller than that for the small ones-in a hard matrix, hence, larger inclusions can initiate voids more easily.

On progressing through Q>T>A sequence, coherency at matrix-inclusions is increased, large inclusions are less potential void nucleators; hence the disappearance of large dimples after slow cooling, higher temperature tempering, irradiation or long term ageing.

It can therefore, be summarised as in Fig. 1.22 that quenched materials suffer from large dimples which are not subdivided by smaller ones, even though carbide particles are present. This is because the critical particle size for fracture is very high in the hard matrix. Tempering, long term ageing or irradiation remove the effectiveness of the inclusions as void nucleators and because of the softened matrix, the critical particle size for void nucleation becomes smaller. Thus, many more finer pores are created at particles, mainly existing on lath-lath packet boundary triple points. Odette and Lucas (1986) reported similar observation in their study of HT-9 (12Cr-1Mo) using RKR model fracture toughness measurements. In their report,
it was shown that the microstructurally-related critical distance parameter in the RKR model does not scale directly with the prior austenite grain size. It was suggested, however, that the feature responsible for causing cleavage fracture in their materials is of the order of the lath packet size. [Odette et al, 1984]. This can be related to the intercarbide spacing since carbides were observed on lath and lath packet boundaries at all heat treatment conditions.

It is therefore possible to relate ductility gain or loss to the dimensions and distribution of dimples or voids formed before and after irradiation. Larger voids will encourage loss of ductility while finer ones will improve it, supported by longer failure times obtained for aged and tempered samples [Table 1.2]. The linear relationship obtained between fracture stress and the reciprocal of the square root of interparticle spacing [Fig. 1.15] is consistent with Honeycombe equation for bainitic steels [Honeycombe, 1983].

\[
\sigma_F = \left( \frac{4E\gamma_p}{(1-\nu)\lambda^2} \right)^{1/2}
\]

where \( \sigma_F \) = fracture stress, \( E \) = Young's Modulus, \( \gamma_p \) = plastic energy, \( \lambda \) = particle spacing and \( \nu \) = Poisson ratio.

5.1.3.1 Yield strength phenomenon

The role of carbide particles in the high temperature fracture process in ferritic/martensitic steels has been well investigated in the present study. A relationship exists between the carbide particle diameter and tensile
yield strength. A critical particle size coincident with peak tensile yield strength (0.01-0.015\,\mu m) can be observed in fig. 3.54. This result agrees with those by Nicholson (1971) where he showed a broad maximum centred at a particle size of a few hundred angstroms. The second phase particles observed are predominantly NbC and M_{23}C_6. It is possible that NbC particles are non-deformable and M_{23}C_6 are deformable in which case an intermediate mechanism in broad agreement with those of Orowan (1948) and Nicholson (1971) can be proposed. Evidence exists to show that the strength of material under study is weakly dependent on particle size, moderately dependent on volume fraction of second phase particles but strongly influenced by the detailed interaction between dislocation and the particle. Fig. 3.55 shows effect of deformation temperature on carbide particle distribution. More critically sized particles are obtained after deformation at 600°C. Fig. 3.56 shows reductions in particle size with increasing cooling rate. This figure indicate particle size at the aircooling range to be within the critical region coincident with peak yield strength [Fig. 3.60]. From Fig. 3.57, it is clear that the water quench range can be associated with smaller particles compared to the oil quench range at that particular tempering and test temperatures [Table 3.18, sample 9]. For aircooled samples tested at 600°C, a linear relationship between yield strength and carbide volume fraction can be observed in fig. 3.62. Fig. 3.63 shows that the tensile yield strength and the reciprocal of the square root of carbide spacing are linearly related for oil quenched samples tested at 600°C. These data are in agreement with Orowan-Ashby expression,

\[ \tau = \frac{(1.2Gb/2.36\pi L)\ln(\frac{\tau}{2b})}{2b} \]

5.1.3
where $\tau = \text{resolved shear stress}$, $G = \text{shear modulus of matrix}$, $b = \text{Burgers vector}$, $L = \text{carbide spacing}$ and $\bar{x} = \text{mean diameter of the circle of intersection between the particle and the slip plane}$. $L = \alpha^{-\frac{1}{2}}$ where $\alpha$ is the number of particles per unit area of the slip plane.

The peak yield strength obtained at the oil quenched range (table 3.18, sample 2) agrees with models by Gladman et al (1971) which predicted a broad yield strength maximum at a critical cooling point.

5.1.3.1a Crack initiation at particle-matrix interface

It is clear that fine carbide particles can be associated with improved total elongation and that fine dimples originated from fine particles [Fig. 3.97]. A critical carbide particle size ($0.0005\mu m$) can be proposed below which carbide particles may not be void nucleators. In Fig. 3.60 it can be observed that total elongation drops exponentially with increase in volume fraction of carbide particles. This data agree with those obtained by Edelson and Baldwin (1962) on copper. Fig. 3.94 shows increasing dimple density as total elongation increases before and after irradiation. This data are supported by those shown in fig. 3.95 where yield strength appears to decrease with increasing dimple density before and after irradiation. Figures 3.89 and 3.96 agree well to show that more larger dimples can be observed at 700°C tempering compared to other tempering range before and after irradiation.

Knott (1980) reported that, shear fractures in quenched and tempered steels appeared to run from carbide to carbide, decohering the carbide-matrix interfaces, rather than cracking
the particles. Such decohesion could arise from the direct
effect of the applied tensile stress or from local stresses
produced by arrays of dislocations which have tangled round
particles. The views of Knott (1980) agrees quite well with
interpretation employed in the present study. During the
plastic straining of a matrix containing carbides, disloca-
tion pile up will produce work-hardening by Orowan-type
mechanism. As the stress on carbide-matrix interface in-
creases with increasing plastic strain; a critical strain
can be reached, at which the interface or particle fractures.
The work of Chen and Knott (1981) show a relationship of
tensile yield strength ($\sigma_y$) critical crack opening displace-
ment ($\delta_i$) and fracture toughness ($K_i$) which can be expressed as

$$K_i = \left( m \sigma_y E \delta_i \right)^{\frac{1}{2}}$$  \hspace{1cm} (5.1.4)

where $m$ is a constant in the range 1.5-3 and $E$ is the Young's
Modulus.

This equation has been employed in the present study to
show, qualitatively, the major microstructural parameters
influencing high temperature failure of ferritic-martensitic
steels. Using a power law of the type

$$\sigma_t = A \varepsilon_t^n$$  \hspace{1cm} (5.1.4a)

where $\varepsilon_t$ = true tensile stress, $\varepsilon_t$ = true tensile strain,
n = strain hardening exponent and $A$ is a dimensional factor
of proportionality with a magnitude of the order of $\frac{Gb}{2\pi}$
where $G$ is the shear modulus and $b$ is the Burgers vector;
logarithmic plots of $\sigma_t$ against $\varepsilon_t$ which are linear
produced slope values representing, $n$, the strain hardening
exponent and the intercepts representing, $A$, the dimensional
factor of proportionality.
From Ashby (1966), the tensile stress acting across the particle/matrix interface, when the matrix is deformed can be written as

\[ \sigma = A \frac{\gamma d}{2b\lambda} \]  \hspace{1cm} 5.1.5

where \( \gamma \) = average shear strain, \( d \) is the diameter of the dispersoid, \( \lambda \) is the dispersoid spacing \( b \) is the Burgers vector and \( A \) is a dimensional factor of proportionality.

From equation 5.1.5, when \( \sigma \) reaches \( \sigma_c \), decohesion can occur and the fracture condition can be expressed as

\[ \sigma_c = A \frac{\gamma_c d}{2b\lambda} \]  \hspace{1cm} 5.1.6

where \( \gamma_c \) = critical shear strain at particle/matrix interface. This Ashby expression is similar to eq. 5.1.1 with \( A = \frac{a}{2b\lambda} \). From eqn. 5.1.6,

\[ \gamma_c = \frac{2b\sigma_c \lambda}{Ad} \]  \hspace{1cm} 5.1.7

From Hahn and Rosenfied (1968)

\[ \gamma = \left( \frac{\delta}{2} \right)/\lambda(n) \]  \hspace{1cm} 5.1.8

where \( \delta \) is the crack opening displacement and \( \lambda(n) \sim \frac{n^2}{40} \) represents the strain hardening exponent. From eqns. 5.1.7 and 5.1.8

\[ \gamma_c = \frac{\delta}{2}/\lambda(n) \]  \hspace{1cm} 5.1.8a
In order to compute $\gamma_c$, it can be assumed

that $\varepsilon(n) = \frac{n^2}{40}$ \hfill \text{[Hahn and Rosenfield (1968)]}

Then,

$$\gamma_c = \frac{\delta_i}{2} \times \frac{40}{n^2}$$

$$= \frac{20\delta_i}{n^2} \quad 5.1.8b$$

Assuming $\gamma_c$ to be 30% of $\gamma$ and $\gamma$ to be 50% of $\varepsilon$, the total strain to fracture, values of $\delta_i$ and $\delta$ can be computed, by substituting values of $n$ obtained from power law plots (eq. 5.1.4a) in eqn. 5.1.8.

$$\delta_i = \frac{n^2 \gamma_c}{20} \quad 5.1.8c$$

and $\delta = \frac{n^2 \gamma}{20} \quad 5.1.8d$

In order to correlate Ashby model to that of Hahn and Rosenfield, from eqn. 5.1.7

$$\gamma_c = \frac{2b\sigma \lambda}{Ad}$$

From eq. 5.1.8b; $\gamma_c = \frac{20\delta_i}{n^2}$

Substituting for $\gamma_c$ in eq. 5.1.7

$$\frac{20\delta_i}{n^2} = \frac{2b\sigma \lambda}{Ad}$$
\[
\delta_i = \frac{2bn^2\sigma_c \lambda}{20Ad}
\]

\[
= \frac{bn^2\sigma_c \lambda}{10Ad}
\]

5.1.8e

\[
A = \frac{Gb}{2\pi}
\]

\[
\delta_i = \frac{\sigma_c n^2 \lambda \pi}{5Gd}
\]

5.1.8f

Taking data obtained for sample 2 in tables 3.18 and 3.25

\[
\sigma_c = 414.7 \text{MNm}^{-2}, \quad \lambda = 1.39 \text{ \mu m}, \quad n^2 = 4.41 \text{MNmm}^{-2}
\]

\[
G = 9107.3 \text{MNm}^{-2}, \quad d = 0.013 \text{ \mu m (experimental)}
\]

hence

\[
\delta_i = \frac{910.0 \times 4.41 \times 10^{-6} \times 1.39 \times 10^{-6} \times \pi}{5 \times 9107.3 \times 0.013 \times 10^{-6}}
\]

\[
= 29.86 \times 10^{-6} \text{ m}
\]

\[
= 29.86 \text{ \mu m}
\]

From eqn. 5.1.8c, obtaining exact \(\gamma_c\):

\[
\gamma_c = \frac{20 \times 29.86 \times 10^{-2}}{4.41}
\]

\[
= 135\%
\]

\(\delta_i\) value obtained for sample 2 in table 3.25 = 160\mu m

(Using Hahn and Rosenfield model eqn. 5.1.8a).
\( \delta_i \) value obtained for sample 2 using combined Ashby model with Hahn and Rosenfield model = 29.86 µm.

Comparison of these two \( \delta_i \) values show some inaccuracies. There is either of two reasons to account for the difference in the two \( \delta_i \) values: (i) Original assumption that \( \gamma = 50\% \) and that \( \gamma_c = 30\% \) can be wrong and (ii) the influence of \( \lambda \) and \( d \) may enhance reductions in \( \delta_i \) values. The second reason may not be appropriate since the values of \( \lambda \) and \( d \) in the calculation are not large enough to cause such large difference in \( \delta_i \) values. The first reason can be appropriate. From \( \gamma_c = 135\% \); if a back calculation is performed, using the original assumption \( \gamma = 50\% \), and \( \gamma_c = 30\% \), then \( \epsilon = 0.909\% \), this is far out compared to 4.8\% obtained by experiment. The correct assumption then can be \( \gamma = 55\% \), and \( \gamma_c = 5\% \) in which case a back calculation given \( \delta_i = 29.86 \) µm will give \( \epsilon = 4.9\% \); which agrees very well with the \( \epsilon \) obtained experimentally.

These discrepancies in \( \delta_i \) values obtained by original assumption (table 3.25) can extend to the \( K_i \) values and \( K_{IC} \) values calculated from Chen and Knott equation. Hence \( \delta_i, K_i \) and \( K_{IC} \) values presented in tables 3.25 and 3.26 are not accurate but convenient to explain the influence of carbide particle and spacing on fracture, toughness. The deduction of the correct assumption is only possible for samples in which \( \lambda \) and \( d \) are known. It can be noted from table 3.23 that only few samples have their \( \lambda \) and \( d \) estimated. In order to apply the correct assumption as predicted earlier and work out correct \( K_i \) and \( K_{IC} \) values, estimation of \( \lambda \) and \( d \) for all samples in table 3.25 is required for further research.
From eqn. 5.1.1
\[
\sigma_T = \alpha \left( \frac{d_{\text{crit}}}{l} \right)
\]
\[
d_{\text{crit}} = \frac{\sigma_T l}{\epsilon \alpha}
\]

From eqn. 5.1.6, \( A = \frac{\alpha}{2k_b \lambda} \)

\[
\frac{\alpha}{\lambda} = \frac{A}{2b \lambda}
\]

\[
A = \frac{G b}{2 \pi} \quad \frac{\alpha}{\lambda} = \frac{G}{2 \pi} \times \frac{1}{2 \lambda} = \frac{G}{4 \pi \lambda}
\]

\[
\frac{\lambda}{\alpha} = \frac{4 \pi \lambda}{G}
\]

\[
d_{\text{crit}} = \frac{\sigma_T}{G \epsilon} \frac{4 \pi \lambda}{4 \pi \lambda} = \frac{\sigma_T}{G \epsilon} \frac{4 \pi \lambda}{4 \pi \lambda}
\]

when \( \sigma_T \) reaches \( \sigma^*_T \), the particle-matrix interface decoheses.

\[
d_{\text{crit}} = \frac{\sigma^*_T}{G \epsilon} \frac{4 \pi \lambda}{4 \pi \lambda}
\]

Consider samples 2 and 11 in tables 3.18 and 3.25.

For sample 2
\( \varepsilon = 23679 \text{ MNm}^{-2}, \quad \gamma_c = 0.06\% \) (based on correct assumption)
\( \sigma^*_T = \sigma_c = 918.0 \text{ MNm}^{-2}, \quad \lambda = 1.39 \text{ \mu m}, \quad \epsilon = 4.8\% \)
\( n^2 = 4.41 \text{ MNm}^{-2}, \quad G = 9107.3 \text{ MNm}^{-2}, \quad \delta_i = 13.49 \text{ \mu m} \)
\( \sigma_y = 398 \text{ MNm}^{-2} \) and \( A = 0.001 \)
Hence

\[ d_{\text{crit}} = \frac{918.0 \times 4 \times 1.39}{9107.3 \times 4.8 \times 10^2} \]

\[ = 0.00037 \text{ \( \mu \)m} \]

\[ = 0.0004 \text{ \( \mu \)m} \]

For sample 11; \( \sigma_1^* = 669.5 \text{ \( MN \)m}^{-2} \), \( \lambda = 0.34 \text{ \( \mu \)m} \)

\( c = 6\% \)

\[ d_{\text{crit}} = \frac{669.5 \times 4 \times 0.34}{9107.3 \times 6 \times 10^2} \]

\[ = 0.00005 \text{ \( \mu \)m} \]

*Conversion from mm to \( \mu \)m.

Comparing \( d_{\text{crit}} \) values for samples 2 and 11 show ten times order of magnitude difference. It can be noted that sample 2 was tested at 500°C and sample 11 at 600°C. This deduction indicates support for test temperature dependence of total elongation and yield strength. Also, it is clear from this \( d_{\text{crit}} \) data that going through Q>T>A \( d_{\text{crit}} \) will decrease as earlier proposed. It is interesting to observe that the calculated \( d_{\text{crit}} \) is consistent with that predicted from experimental data.
5.2.4.0 Solute element segregation

During quenching or cooling above a critical rate, vacancy gradients develop in the vicinity of effective sinks as the material attempts to achieve the new equilibrium vacancy concentration. If solutes are present, which exhibit strong binding energies (i.e., larger than thermal energy, $\frac{3}{2}kT$) with vacancies; the vacancy flux induces a coupled non-equilibrium solute flux. This leads to solute segregation at vacancy sinks such as interfaces in the microstructure (Anthony, 1969). According to McLean (1962) equilibrium segregation theory states "For an impurity with binding energy to the lattice, $E_b$, at any temperature, $T$, there will be an increased concentration of that impurity in a monolayer on interfaces, $C_b$." The driving force for this being the reduction of energy, $E_b$, of the impurity, on placing it in a strain-free environment on the interface.

5.2.4.1 Evidence for solute segregation

Clear evidence has been obtained, both theoretically and experimentally, to show solute element segregation on interfaces in ferritic-martensitic steels. From the theoretical computer modelling of solute segregation; it was observed that the extent of segregation depends on three variables, i.e., the solution treatment temperature, ageing time and temperature; and cooling rate at which material tends to attain new equilibrium structures. Two and three dimensional plots obtained showed that solute elements such as silicon, molybdenum, boron, vanadium and niobium can segregate to effective interfaces in ferritic/martensitic steels depending on the three variables mentioned earlier. [Figs. 2.24-2.35]. In figures 2.26 and 2.27, molybdenum segregation show peaks after ageing at 650°C for about half an hour, whereas,
ageing at 600°C produced molybdenum peaks after one hour. From figures 2.25 and 2.27, silicon and molybdenum peak segregation can be predicted at about 20-30°C per second cooling rate. Theoretical prediction about boron segregation is sceptical. The difficulties in obtaining a clear prediction of boron segregation arise from lack of acceptable binding energy data for boron and that of activation energy for diffusion. However, figures 2.30 and 2.31 show appearance of boron segregation at water quench range for a shorter ageing time. No clear data were obtained for boron from the autoradiography technique.

Chromium is a principal alloying element in the material under investigation, hence its segregation to interfaces can be expected. Chromium segregation peak can be obtained at a faster cooling rate when ageing temperature is increased. Constant ageing temperature varied cooling rate can cause chromium segregation to occur at longer ageing time. Possible reasons that can be advanced for large chromium segregation include the lack of nucleation sites for chromium carbide participation. Since nucleation sites increase as we go to higher tempering, chromium segregation tends to diminish and large precipitation of chromium based carbides can be observed on interfaces [figs. 1.7 and 1.8].

Experimental evidences have been obtained to show that solute segregation can occur in 12Cr martensitic steels at cooling rates of 6.5°C, 50°C and 220°C per second following austenitisation. Silicon and molybdenum atoms in particular, participate in vacancy-coupled diffusion to lath and lath packet boundaries [Figs. 2.36 and 2.37]. The absence of any of these atoms on a proportion of lath boundaries is not unexpected. This can be due to variations in boundary sink strength which is a factor of boundary angular misorientation and other geometrical factors.
Silicon is an undersize solute in α-iron with a misfit of -0.057. The binding energy between a vacancy and a silicon atom in the ferrite has been estimated as 0.202eV [Faulkner, 1985]. This relatively strong binding energy is thus qualitatively consistent with the observed segregation behaviour of silicon in ferritic/martensitic steels [Faulkner, Shaefer, Adetunji and Little, 1987]. This behaviour is in agreement with data on microstructural evolution in 12%Cr steels, under fast reactor irradiation, in which substantial incorporation of silicon into irradiation-induced precipitate is observed; and for which explanations based on non-equilibrium solute segregation have been advanced. [Little et al, 1982]

Molybdenum is an undersize solute in α-iron with a misfit of +0.095. The molybdenum-vacancy complex is a faster diffuser than matrix iron. Molybdenum, nickel, vanadium and boron are remedial elements in which case their segregation can be due to synergistic coupling with elements such as silicon, phosphorus, manganese and sulphur [Seah (1980), Guttman (1977)]. This idea cannot be substantiated, hence, it could rather be believed that elements segregate according to their chemical properties. For example, nickel segregation has been largely observed in the present study as well as by Clausings et al (1986) in their investigation of radiation-induced segregation in HT-9 (12Cr-1Mn). Interpretation of nickel segregation, in view of current theories is still not clear. The idea of solubility variation with enrichment ratios (Hume-Rothery rule) can be considered to explain massive nickel segregation to interfaces. Nickel, being a γ-stabiliser with minimum solubility in α-iron can segregate to higher energy interfaces depending on parameters such as cooling rate, ageing time and temperature. Another explanation by Clausings et al (1986)
suggests that traces of γ-phase may be present as a residue at prior austenite grain boundaries. Gelles (1982) suggested the possibility of nickel silicide phase (Ni3Si) being formed on interfaces; but in this present study, precipitate-free interfaces were investigated and excess concentration of nickel was observed on lath and lath packet boundaries.

Further work is clearly required to obtain an acceptable explanation for nickel's behaviour. It can be suspected that the molybdenum segregation may be influenced by the chromium content of material under study. It is possible that the large composition of chromium and its higher affinity for carbon than molybdenum has influenced molybdenum segregation to lath boundaries. The role of molybdenum in phosphorus-induced temper embrittlement of 12% Cr steels was reported by Guillou, Guttmann and Dumoulin (1981). Dumoulin et al (1980) investigated molybdenum beneficial effects in martensitic steels. It was suggested that molybdenum partially inhibits the segregation of phosphorus by tying it up in the grain interior due to the strong Mo-P affinity and that molybdenum segregation to grain boundaries counteracts the embrittling action of the segregated phosphorus. Yu et al (1980) observed similar features in 2.25Cr-1Mo steels.

However, phosphorus is not present in material under study, it is possible that other solute elements may be playing similar role to that of phosphorous, and hence, cause the dragging of molybdenum to lath and lath packet boundaries. Silicon is a likely element which can do this. It is interesting to observe the co-segregation of molybdenum and silicon on lath boundaries in ferritic/martensitic steel. Another reason that can be advanced for molybdenum
segregation comes from the fact that molybdenum reaction rate can be retarded as carbon comes out of solution [Gessel et al, 1977]. According to Kasen (1983) segregation of solutes to grain boundaries can be as a result of solute acquisition by migrating boundaries during recrystallization and grain growth. Fig. 1.5b showed evidence for boundary migration in an oil quenched sample tempered at 750°C. Since it has been shown that segregation of solutes diminish with increasing tempering temperature, both experimentally and theoretically, it is not likely that Kasen's view is appropriate in this case.

It is interesting to know that segregation peaks of silicon and molybdenum are obtained at the oil quench range (50°C/sec) which on comparison with the theoretical prediction (20-30°C/sec) show consistent agreement [Fig. 2.36b and 2.36c].

Theoretical predictions [Faulkner, 1987] of solute concentration as a function of cooling rate and tempering time at 600°C from a model based on combined equilibrium and non-equilibrium segregation mechanism also showed trends which imply that strong silicon enrichment occurred at 50°C per second cooling rate followed by ageing (~1hr) at 600°C. These data are in broad agreement with microanalytical data obtained in the present study.

A comparative study of analytical equipments was undertaken to show efficiency of analytical electron microscopy in the determination of solute segregation. In the present study, two equipments were used to obtain segregation data; the FEGSTEM (HB501) and the STEM (JEOL-100CX). The FEGSTEM (HB501) was found as a better instrument producing more accurate microanalytical data than the STEM (JEOL-100CX). The deficiency of the STEM (JEOL-100CX) can be associated
with limitations in spatial resolution, beam current, astigmasors and the probe size. Higher spatial and image resolution is possible in the FEGSTEM (HB501) because of its smaller probe size, larger beam current, and powerful astigmasors. The larger probe size in the STEM (100CX) makes it less possible to analyse lath boundary characteristics accurately.

5.2.4.2 Calculation of detection limit in FEGSTEM

From the relation \( i = \frac{\pi^2 \beta \alpha^2 d^2}{4} \) where

\( i \) is the maximum current, \( d \) is the diameter of probe, \( \beta \) is the brightness, ie. current density per unit solid angle \((\text{A cm}^{-2} \text{ Sr}^{-1})\) and \( \alpha \) is the semi-angle of probe-forming lens; larger \( \beta \) value of the FEGSTEM will enhance very much larger current to produce better x-ray detection [Titchmarsh, 1987]. It can also be noted that energy that can be applied on FEGSTEM (HB501) is about 1,000 times that of STEM (100CX).

However, in order to obtain a more qualitative account of comparison between FEGSTEM (HB501) and STEM (100CX); it is useful to employ some beam spreading calculations for both systems. Fig. 2.50 is a sketch of beam spreading on the thin foil surface for STEM (100CX) and FEGSTEM (HB501). If the probe sizes for the STEM (100CX) and FEGSTEM (HB501) are 140Å and 10Å respectively, and the beam spread on the surface of a foil, about an interface of interest are 550Å and 400Å for STEM and FEGSTEM, respectively.

Assuming the thickness of impurity layer, perpendicular to foil to be 20Å.
Volume of layer = 20 x 1000 x 200 (FEGSTEM)

= (20 x 1000 x 200) + (150 x 1000 x 20) (STEM)

Volume of excited material = \( \frac{1}{3} r^2 h = 4 \times 10^7 \) (FEGSTEM)

and \( \frac{h}{3} (R^2 + Rr + r^2) = 1000 (7562 + 20625 + 5625) = 1 \times 10^8 \) (STEM)

Assuming atomic volume layer is same as in the matrix

Apparent concentration of impurity = \( \frac{\text{Vol. of layer}}{\text{Vol. of excited material}} \)

\[
= \frac{4 \times 10^6}{4 \times 10^7} = 10\% \quad \text{(FEGSTEM)}
\]

\[
= \frac{7 \times 10^6}{1 \times 10^8} = 7\% \quad \text{(STEM)}
\]

Assuming limit of detectability for medium atomic number elements in STEM to be 1.0%

Improvement in detectable limit = \( \frac{\sqrt{N_2}}{N_1} \)

where \( N_1 = \) count rate in STEM \( = 1 \)
\( N_2 = \) count rate in FEGSTEM \( = 1000 \)

Therefore improvement = \( \frac{1}{\sqrt{1000}} = \frac{1}{31.6} = 0.032\% \)

The minimum detectable limit in FEGSTEM is approximately 0.032%. This means that all measurements of concentration above \( \sim 0.032\% \) should be significant compared to limit of 1.0 wt% in the STEM. In a foil 1000Å thick, these detection limits should be sufficient to detect a layer of impurity 20Å wide on a boundary. In the case of FEGSTEM, the apparent,
concentration is 300 times the detection limit whereas for the STEM, it is 7 times the detection limit.

Therefore, based on this consideration the FEGSTEM offers an improved sensitivity of a factor of 40 times over that of the STEM in lath boundary segregation detection [Faulkner, 1987]. In figures 2.47 - 2.43a, large deviation can be observed in STEM (100CX) data compared to that of the FEGSTEM, which is not unexpected, since this is also indicated in the beam spread calculation that useful microanalytical work by EDX method cannot be achieved without large enough probe current to excite a useful signal. The larger the current, the better improved sensitivity of detection.

Segregation profiles constructed for particular lath boundaries in a water quenched sample using both systems indicate clear inaccuracies in limits of detection [Figs. 2.41-2.43].

5.2.5.0 Solute segregation related to mechanical behaviour

It has been one of the major aims of this present study to relate solute segregation to high temperature mechanical behaviour. It can be noted that segregation study was conducted on materials upon which heat treatment I was applied, while the mechanical property data in comparison were obtained from similar materials upon which heat treatment II was applied.

However, plastic deformation temperature are similar in both cases.
5.2.5.1 Embrittlement processes

This section can be treated under three subheadings (i). High temperature fracture before irradiation (ii) High temperature fracture after irradiation and (iii) Strain rate dependence of fracture toughness; and explained in terms of (i) solute segregation (ii) void nucleation and (iii) irradiation effects.

5.2.5.1.1 Fracture before irradiation

In section 5.1.3.0 of this thesis, it was highlighted that segregation of impurities to interfaces can be one among other mechanisms by which fracture can initiate. From present data, enhanced segregation of silicon and molybdenum can play some beneficial role in high temperature mechanical behaviour of 1.4914 steels.

If fracture is considered to initiate by a microcrack formation along lath boundaries, the fracture energy, can be related to the local stress $\sigma_b$, required to propagate a crack of length, $c$, according to a modified Griffith criterion,

$$\sigma_b = \left( \frac{2E\gamma}{\pi c} \right)^{\frac{1}{2}}$$  \hspace{1cm} 5.21

where $E$ is the Young's Modulus, $\gamma' = \gamma + \gamma_p$ is the cohesive energy or total energy required per unit increase in crack area, comprising $\gamma$, the true surface energy and $\gamma_p$, the plastic work done at the moving crack tip. The role of silicon and molybdenum segregation in increasing $\sigma_b$ and the fracture energy can be explained in terms of their actions, in enhancing the interfacial cohesive energy, the $\gamma'$ value for lath boundaries [Faulkner, Schaefer, Adetunji and Little (1987)]. This enhancement would arise from
contributions to both $\gamma$ and $\gamma_p$, according to the arguments of McMahon and Vitek (1979).

Comparing Ashby relation (eq. 5.1.1) to the modified Griffith relation (eq. 5.2.1); since evidence exists for solute segregation to interfaces; $\sigma_a$ can no more be constant; then $\sigma$ changes in equal proportions with $\sigma_a$ and by combining eqn. 5.1.1 and 4.2.1, we can write

\[
\left( \frac{2E}{\pi c} \right)^{\frac{1}{2}} = \frac{d_{\text{crit}}}{\lambda} \quad \text{5.2.2}
\]

\[
\frac{2E\gamma'}{\pi c} = \frac{\alpha^2 \varepsilon^2 (d_{\text{crit}})^2}{\lambda^2} \quad \text{5.2.3}
\]

\[
\varepsilon^2 = \frac{2E\gamma' \lambda^2}{\alpha^2 d_{\text{crit}} \pi c} \quad \text{5.2.3}
\]

\[
\varepsilon^* = \frac{\lambda (2E\gamma')^{\frac{1}{2}}}{\alpha d_{\text{crit}} \sqrt{\pi c}} = \frac{\lambda}{\alpha d_{\text{crit}}} (2E\gamma')^{\frac{1}{2}} \quad \text{5.2.4}
\]

where $\varepsilon^*$ is the critical strain at the interface to open a crack of length $c$.

Furthermore, from eqs. 5.1.6 and 5.1.1

\[
\frac{\alpha}{\lambda} = \frac{A}{2b\lambda} \quad \text{and} \quad A = \frac{Gb}{2\pi}
\]

\[
\frac{\alpha}{\lambda} = \frac{Gb}{2\pi} / 2b\lambda = \frac{G}{4\pi \lambda} \quad \text{5.2.4a}
\]
From eq. 5.2.4

\[ \varepsilon^* = \frac{4 \pi \lambda}{Gd_{\text{crit}}} \left( \frac{2E\gamma'}{\pi c} \right)^{\frac{1}{2}} \]

consider specimen 2; an oil quenched sample in which strong silicon and molybdenum segregation was observed. If \( c = 1 \mu m \);

\[ \lambda = 1.39 \mu m \quad G = 9107.3 \text{ MNm}^{-2} \]
\[ E = 23679 \text{ MNm}^{-2} \quad \gamma = 4 \text{ Nm}^{-2} \]

\[ \gamma' = \gamma_p + \gamma \]

[McMahon and Vitek (1979)]

\[ \gamma_p = 15\gamma \]

hence, \( \gamma' = 16\gamma \)

and \( \varepsilon^* = \left( \frac{4\pi \times 1.39}{9107.3 \times 0.004} \right) \left( \frac{2 \times 23679 \times 16 \times 4 \times 10^{-6}}{\pi \times 1 \times 10^{-6}} \right)^{\frac{1}{2}} \)

\[ = 0.479 (982.2 \times 10^{-2}) \]
\[ = 470.9 \times 10^{-2} \]
\[ = 4.71\% \]

This \( \varepsilon^* \) value obtained from calculation is in broad agreement with the experimental data of 4.8\% [Table 3.18].

From this deduction, it is clear that \( \varepsilon^* \) is governed by \( \gamma' \). Large \( \gamma' \) can cause large \( \varepsilon^* \); in which case, the argument of beneficial role of silicon and molybdenum segregation in enhancing \( \gamma' \), the cohesive energy can be documented. It is interesting to observe peak total elongation and yield strength trough coincident with peak silicon and molybdenum segregation at the oil quench range for samples tested at 600\(^{\circ}\)C. [Figs. 2.46 and 2.47]
5.2.5.1.2 Fracture after Irradiation

Irradiation influence on fracture can be rationalised in terms of radiation embrittlement which can occur based on two processes; (i) irradiation hardening of the matrix and (ii) helium embrittlement. Irradiation hardening can be influenced by (i) increase density of interstitial clusters in the presence of small levels of nitrogen or carbon atoms and (ii) irradiation-induced segregation or precipitation on interfaces. Nickel silicide, a radiation-induced precipitate on grain boundaries can influence intergranular fracture.

It is also known that helium gas can be generated via \( (n, \alpha) \) reaction by boron during irradiation. These gas bubbles can coalesce and grow forming large cavities. Hence, it is possible to rationalise helium embrittlement in terms of void coalescence mechanisms. [McMahon and Vitek (1979)]. Both helium embrittlement and irradiation hardening can be explained using derivation 5.2.4. The presence of nickel silicide precipitate on the grain boundary will cause large reductions in \( \gamma \) and \( \gamma_p \), hence, \( \gamma' \). Then, the lower the \( \gamma' \) the smaller the \( \epsilon^* \), the critical strain effective on the interface; and the more catastrophic the fracture will be. However, in the present study, it is not expected that embrittling phase like nickel silicide can be formed based on the irradiation temperature employed. It is expected that helium bubbles will be formed, but that their sizes will be small and that they are well dispersed throughout the microstructure. Consider small helium bubbles which are over pressurised as small particles or small voids which cannot grow; the Ashby modified Griffith derivation can be applied to show that smaller and well dispersed helium bubbles will enhance large \( \epsilon^* \), thereby improving total
elongation - in the same manner finer carbide particles would. It is not impossible that helium bubbles can influence crack nucleation when they are strung along grain boundaries during plastic deformation. If the smaller bubbles behave like smaller particles in their over-pressurised state, dislocations can bow around them until a critical strain is reached and crack can be initiated.

It appears to be the case in the present study, in that, improved total elongation was observed for all samples, not withstanding the presence of helium bubbles.

These ideas agree quite well with those of King and Knott (1981) and Chen and Knott (1981). Another supporting evidence is the observation of Wassilew (1983) and Little (1982) that no significant void swelling are present in ferritic-martensitic steel and that fracture occurred purely intergranular. If a wholly ductile fracture process governed by nucleation and coalescence of microvoids at particles (eg. carbides) is considered, the fracture energy is related to plastic strain, \( \varepsilon \) contributions required to nucleate and grow the microvoids. The void nucleation strain can be written as

\[
\varepsilon = \left[ \frac{2(1-v)}{\pi Gd} \right]^{\frac{1}{2}} \tag{5.2.5}
\]

[Smith and Barnby (1967); King and Knott (1981)]

where \( \lambda \) and \( d \) are the particle spacing and diameter respectively, \( G \) is the shear modulus \( v \) is the Poissons ratio and \( \gamma' \) is now the particle-matrix cohesive energy. Increases in fracture energy can therefore be explained by enhancement of \( \gamma' \) due to segregation of silicon and molybdenum at particle-matrix interfaces.

Note: Equation 5.2.5 is same as 5.2.46 and that on p.30.
Enhancement of $\varepsilon$ can be deduced for when there is no segregation, $\gamma'$ will be constant and $\eta$ becomes an important parameter as earlier discussed in this thesis. If the particle diameter is fine, large $\varepsilon$ will be required for nucleation and growth of microvoids and hence imply better ductility of material under investigation.

In order to rationalise, qualitatively, the influence of helium bubbles on total elongation and high temperature failure, model calculation of helium bubble size can be undertaken.

For helium bubbles under tension

$$p = \frac{2\gamma}{r}$$

where $p$ = pressure, $\gamma$ = interfacial energy and $r$ is the bubble radius.

Eqn. 5.2.5a can also be expressed as

$$\sigma_T = \frac{2\gamma}{r}$$

where $\sigma_T$ = tensile stress at fracture

consider irradiated sample 11

with $\sigma_T = 435.6$ MNm$^{-2}$

taken $\gamma = 4$ Nm$^{-2}$

$$r = \frac{2\gamma}{\sigma_T}$$

$$\frac{2 \times 4 \times 10^{-6}}{435.6} = .018 \times 10^{-6} \text{m}$$

$$= 0.018 \mu \text{m}$$
diameter \( (d) = 0.037 \, \mu m \)  
Helium bubble diameter \( = 0.037 \, \mu m \)

For irradiated sample 11, taking dimple diameter to be ten times particle diameter, it can be assumed that mean carbide particle diameter after irradiation = 0.324 \( \mu m \) (table 3.21).

Effective mean diameter = \( d_{\text{crit}} + d_{\text{mean}} \)

\[
d_{\text{crit}} \text{ (after irradiation)} = \frac{\sigma \sqrt{4\pi \lambda}}{G \varepsilon}
\]

\[
= \frac{435.6 \times \pi \times 4 \times 5.2}{9107.3 \times 13.97 \times 10^3}
\]

\[
= 0.00022 \, \mu m
\]

Effective mean diameter = 0.3242 \( \mu m \)

If pressurised helium bubbles behave like spherical particles during plastic deformation, effective particle diameter on the microstructure will be

\[
\left( \frac{0.3242 + 0.037}{2} \right) = 0.181 \, \mu m
\]

Using equation from McMahon et al (1979)

\[
\varepsilon = \lambda \left\{ \frac{2(1-\nu)\gamma'}{\pi G d} \right\}^{\frac{1}{2}}
\]

\[
\varepsilon^2 = \frac{\lambda^2 2(1-\nu)\gamma'}{\pi G d}
\]

If \( \lambda = 5.2 \mu m \quad G = 9107.3 \, MNm^{-2} \quad d = .18 \, \mu m \)
Taking $\gamma = 4 \times 10^{-6}$ MNm$^{-2}$

$\gamma' = \gamma + \gamma_p$, $\gamma_p = \text{plastic energy and } \gamma = \text{interface energy}$

$\gamma_p = \gamma _{15}$ [McMahon and Vitek (1979)]

$\gamma' = 16 \gamma = \text{particle-matrix cohesive energy}$

Then

$$
\varepsilon^2 = \frac{(5.2)^2 \times 2 \times (7) \times 16 \times 4 \times 10^{-6} \times 10^{-12}}{\pi \times 9107.3 \times 0.181 \times 10^{-6}}
$$

$$= 0.468 \times 10^{-12}
$$

$$\varepsilon = 0.68 \%$

Comparing the deduced $\varepsilon$ value of $0.68\%$ to that from experiment of $13.97\%$ indicates some influence of helium bubble on total elongation and fracture behaviour. It is interesting to obtain calculated $\varepsilon$ value showing no agreement with the one obtained by experiment. Further investigation of helium bubble size, distribution density and fraction is required in order to obtain an accurate assessment of helium bubble influence on fracture behaviour of ferritic/martensitic steels.

5.2.5.1.2a Estimation of Void Swelling

Assuming ideal gas behaviour.

Molar volume $= 0.02241$ m$^3$ mol$^{-1}$

Boltzmann constant $(k) = 1.38 \times 10^{-23}$ J K$^{-1}$
Avogadro number \( = 6.022 \times 10^{23} \)

Volume of one He atom \( = \frac{0.02241}{6.022} \times 10^{-23} \text{ m}^3 \)

\[ = 3.72 \times 10^{-26} \text{ m}^3 \]

Consider sample 2

He bubble radius \( = 0.0135 \text{ mm} = 0.0135 \times 10^{-6} \text{ m} \)

Assume spherical shape of bubbles

Bubble volume \( = \frac{4}{3} (0.0135 \times 10^{-6})^3 \text{ m}^3 \)

\[ = 1.03 \times 10^{-23} \text{ m}^3 \]

Number of atoms in a bubble \( = \frac{1.03 \times 10^{-23}}{3.72 \times 10^{-26}} \)

\[ = \frac{1.03 \times 10^{-23}}{0.00372 \times 10^{-23}} \]

\[ = 277 \]

From equation 1.020

\[ \frac{\Delta V}{V} = \left(\frac{3}{4} \pi\right)(\frac{\text{Ind}}{545 \gamma})^{\frac{3}{2}} \]

\( T = 273.2 \text{ K}, \) assume \( d = 5 \mu \text{m}, \ n = 277, \ \gamma = 4 \text{j m}^{-2} \)

\[ \frac{\Delta V}{V} = \frac{3\pi}{4} \left(\frac{273.2 \times 277 \times 5 \times 10^{-6}}{546 \times 4}\right)^{\frac{3}{2}} \]

\[ (\Delta V/V)^2 = \left(\frac{3\pi}{4}\right)^2 (173.25 \times 10^{-6})^3 \]

\[ = \left(\frac{3\pi}{4}\right)^2 (5200196.2 \times 10^{-18}) \]
\[
\frac{\Delta V}{V} = \frac{3\pi}{4} \times (0.2280.39 \times 10^{-9})
\]

\[
= 5373 \times 10^{-9}
\]

\[
= 5.373 \times 10^{-6}
\]

\[
= 5.373E-4\%
\]

Void swelling values are computed using the above calculations for all irradiated samples (Table 3.19).

These deductions are very important technologically, since bubble size ranges can be design parameters to obtain improved void swelling resistance of materials under irradiation. The values obtained show agreement with reports by Little et al (1979), Wassilew (1983), Klueh et al (1983), Gelles (1981) and Stamm et al (1987). From the calculated void swelling data, assumption of same bubble spacing of 5\(\mu\)m give higher values as bubble radius increases. It is interesting to observe increasing helium bubble radius and the resultant increase in void swelling for samples tested at 650°C. However, the constant bubble spacing assumed may not be practicable since variation in bubble spacing is possible as test temperature increases. It was shown that helium concentration is a function of bubble size; the larger the concentration, the smaller the size of the matrix bubbles [Adetunji, 1985].

For the helium concentration of 52.7 appm and the He/dpa ratio of 308 observed in the present study, the bubble size range obtained can be appropriate.
5.2.5.1.3 Strain rate dependence of fracture toughness
Charpy impact energy data obtained by Schaefer et al (1986) for material under investigation showed peak fracture energy at the oil quench range. It can be suggested that the presence of silicon and molybdenum on lath boundaries increases the energy absorbed at fracture [Figs. 2.45 and 2.46]. This observation of peak silicon and molybdenum segregation coincident with peak absorbed fracture energy is interesting in that Schaefer's impact data was obtained at higher strain rate and high temperature whereas materials for which segregation data was obtained, were fractured at lower strain rate ($10^{-4}$ S$^{-1}$) and high temperature.

From the fracture toughness obtained (Tables 3.25 and 3.26) before and after irradiation it can be deduced that fracture toughness is dependent on strain rate. Consider sample 2 in table 3.18, an oil quenched sample in which strong segregation of silicon and molybdenum was observed, taking time to fracture = 635.5 seconds, total elongation = 4.8%,

\[
\text{Strain rate} = \frac{4.8}{635.5} = 7.6 \times 10^{-3} \text{ S}^{-1}
\]

Calculated $K_{IC} = 39.6 \text{ MNm}^{-2}$ (Table 3.25)

Similarly, sample 1 in table 3.18:

Time to fracture = 569 seconds, total elongation = 4%

\[
\text{Strain rate} = \frac{4}{569} = 7.03 \times 10^{-3} \text{ S}^{-1}
\]

\[
K_{IC} = 22.8 \text{ MNm}^{-2}
\]

Also sample 8 in which no segregation can be observed, time to fracture = 915 seconds, total elongation = 6.8%

\[
\text{Strain rate} = \frac{6.8}{915} = 7.43 \times 10^{-3} \text{ S}^{-1}; \ K_{IC} = 22.9 \text{ MNm}^{-2}
\]
Comparing sample 2 in which strong segregation of silicon and molybdenum were observed and sample 8 in which no segregation occurred; it can be proposed that silicon and molybdenum segregation influence fracture toughness.

From samples 2, 1 and 8, calculated data indicate variation of fracture toughness with strain rate.

It can therefore be noted that lower strain rate employed in the present study can be associated with large work hardening observed before and after irradiation.
5.3.6.0 Quenching rate data

Experimental data indicate cooling rates for air, oil and water quenchings as -47, -115 and -345.5°C per second respectively. From the cooling curves [Figs. 3.50-3.52], there is a decrease in cooling rate with time. This is due to sharp heat loss from the hot specimen.

According to Newton's Law of cooling, as the temperature gradient between specimen and fluid decreases, there should be a decrease in the rate of heat transfer. In order to show the degree of accuracy obtained in this investigation, theoretical calculations can be considered.

5.3.6.1 Air cooling rate calculation

Applying McAdams equations when average air thermal conductivity:

\[ K = 41.74 \times 10^{-3} \text{ Wm}^{-1} \text{K}^{-1} \]

average air density, \( \rho = 1.162 \text{ Kgm}^{-3} \)

average air viscosity, \( \mu = 27.34 \times 10^{-6} \text{ Kg m}^{-1} \text{s}^{-1} \)

Constant pressure specific heat of air, \( C_p = 1.054 \times 10^3 \text{ JKg}^{-1} \text{m}^{-1} \text{s}^{-1} \)

Temperature difference, \( \Delta T = 600^\circ\text{C} \)

Gauge length, \( L = 0.212 \text{m} (21.2 \times 10^{-3} \text{ m}) \)

From \( Pr = \frac{\mu C_p}{K} \)

we have \( Pr = \frac{27.34 \times 10^{-6} \times 1.054 \times 10^3}{41.74 \times 10^{-3}} = 0.69 \)
\[
Gr = \frac{\beta^2 \Theta L q^3}{\mu^3}
\]

\[
= \frac{(1.162)^2 (600)(21.2 \times 10^{-3})^3 \times 9.806}{(27.24 \times 10^{-6})^2}
\]

\[
= 1.013 \times 10^8
\]

\[
(PrGr) = 0.69 \times 1.013 \times 10^8
\]

\[
= 0.698 \times 10^8
\]

Using \( Nu = 0.69 \ (PrGr)^{\frac{1}{4}} \) satisfies the condition
\( 10^4 < (PrGr) < 10^9 \) for laminar flow [McAdams, 1957]
we have
\[\]
\[
Nu = 0.69 \times (0.698 \times 10^8)^{\frac{1}{4}}
\]

\[
= 63.1
\]

but \( Nu = \frac{hL}{k} \). \( \therefore h = \frac{41.74 \times 10^{-3} \times 63.1}{21.1 \times 10^{-3}} \)

\[
= 124.2 \text{ Wm}^{-2} \text{ K}
\]

From \( \frac{1}{U} = \frac{1}{k} + \frac{1}{h} \) where \( x = \) specimen thickness

\[
k = \text{thermal conductivity of material}
\]

\[
\frac{1}{U} = \frac{0.55 \times 10^{-3}}{37.2} + \frac{1}{124.2}
\]

\[
= 0.00806
\]

\[U = 124.01 \text{ Wm}^{-2}\]

From \( \dot{Q} = UA (T_s - T_w) \) where \( A = \text{surface area} \)

\[
= 124.01 \times 89.92 \times 10^{-6} \times (620 - 20)
\]

\[
= 6.68, \text{watts}
\]
The heat capacity of the gauge area where

\( V_g = \) volume of gauge section
\( C_{p_g} = \) heat capacity of gauge section
\( \rho = \) density of alloy

can be written as

\[
C_{p_g} = C_{p\text{alloy}} \times V_g \times \rho_{\text{alloy}}
\]

\[
\rho_{\text{alloy}} = 7833 \text{ kg m}^{-3}; C_{p\text{alloy}} = 323.4 \text{ J/kgK}
\]

\[
C_{p_g} = 323.4 \times 49.38 \times 10^{-9} \times 7833
\]

\[
= 0.125 \text{ J/K}
\]

\( \dot{R} = \) initial cooling rate of the gauge length

\[
\dot{R} = \frac{Q}{C_{p_g}} = \frac{6.68}{0.125}
\]

\[
= -53.4 \text{ K/sec.}
\]

5.3.6.2 Oil quenching (Medium viscosity SAE59)

By McAdam's equation

\[
Pr = \frac{\mu C_P}{K}; Gr = \frac{\rho^2 \theta L^3}{\mu^2}
\]

\[
Nu = \frac{hL}{K}
\]
Conditions \( \text{Nu} = 0.69(PrGr)^{\frac{1}{2}}; \ 10^4 < (PrGr) < 10^9 \) - Laminar

\( \text{Nu} = 0.129(PrGr)^{\frac{1}{3}}; \ 10^9 < (PrGr) < 10^{12} \) - Turbulent

(McAdams, 1957)

\( \Theta = 600^\circ C \)

\( K = 0.145 \text{ Wm}^{-1}\text{K}^{-1} \) for oil

\( \mu \text{ at } 20^\circ C = 0.799 \text{ kg m}^{-1} \text{ s}^{-1} \)

\( \rho \text{ at } 20^\circ C = 88.23 \text{ kg m}^{-3} \)

\( \text{Cp at } 20^\circ C = 1.88 \times 10^3 \text{ J kg}^{-1}\text{K}^{-1} \)

Gauge length = 21.2 x 10^{-3} m

\( Pr = 10100 \); \( Gr = \frac{(888.23)^2(600)(21.2)^3 \times 9.806}{(0.799)^2} \)

\( Pr = 1.01 \times 10^4 \); \( Gr = 6.93 \times 10^4 \)

\( (PrGr) = 6.99 \times 10^8 \)

\( \text{Nu} = 0.69(PrGr)^{\frac{1}{2}} = 0.69 \ (6.99 \times 10^4)^{\frac{1}{2}} = 1.122 \times 10^2 \)

but \( \text{Nu} = \frac{hL}{K} \)

\( h = \frac{\text{NuK}}{L} \)

\( = \frac{112.2 \times 0.145}{21.2 \times 10^{-3}} \)

\( = 767.4 \text{ Wm}^{-2} \text{ K}^{-1} \)
\[
\frac{1}{U} = \frac{0.55 \times 10^{-3}}{37.2} + \frac{1}{767.4}
\]

\[
U = 758.9
\]

\[
\dot{Q} = UA(T_s - T_w)
\]

\[
= 758.9 \times 89.82 \times 10^{-6} (600)
\]

\[
= 40.89 \text{ watts}
\]

\[
\dot{R} = \frac{-40.90}{0.125} \text{ K/sec}
\]

\[
= -327 \text{ K/sec}
\]

5.3.6.3 Water quenching rate calculation

Using the same approach [McAdams, 1957]

\[
Pr = \frac{\mu c_p}{K} ; Gr = \frac{\rho 20L^3 q}{\mu^2}
\]

\[
\theta = 600^\circ \text{C}
\]

\[
K \text{ for water at } 22^\circ \text{C} = 0.603 \text{ Wm}^{-1} \text{ K}^{-1}
\]

\[
\mu \text{ for water at } 22^\circ \text{C} = 9.58 \times 10^{-4} \text{ Kg m}^{-1} \text{ s}^{-1}
\]

\[
C_p \text{ for water at } 22^\circ \text{C} = 4180 \text{ J/Kg/K}
\]

\[
\rho \text{ for water at } 22^\circ \text{C} = 997.82 \text{ Kg m}^{-3}
\]

\[
L = 21.2 \times 10^{-3}
\]

\[
g = 9.8066 \text{ m s}^{-2}
\]

\[
Pr = 6.64
\]

\[
Gr = \frac{(997.82)^2(600)(21.2)^3 \times 10^{-9} \times 9.8066}{(9.58 \times 10^{-4})^2}
\]

\[
= 6.08 \times 10^{10}
\]
\[
(PrGr) = 6.08 \times 10^{10} \times 6.64
\]
\[
= 4.04 \times 10^{11}
\]
\[
Nu = 0.129 (PrGr) = 0.129(0.404 \times 10^{12})^{\frac{1}{3}}
\]
\[
= 0.0954 \times 10^4
\]
\[
Nu = 954
\]
\[
h = \frac{NuK}{L} = \frac{954 \times 0.603}{21.2 \times 10^{-3}}
\]
\[
= 27134 \text{ Wm}^{-2} \text{K}^{-1}
\]
\[
1 \over U = \frac{x}{K} + \frac{1}{h}
\]
\[
= \frac{0.55 \times 10^{-3}}{37.2} + \frac{1}{27135}
\]
\[
= 0.000052
\]
\[
U = 19230.76 \text{ W m}^{-2} \text{K}^{-1}
\]
\[ Q = UA (T_S - T_W) \]
\[ = 19230.76 \times 89.82 \times 10^{-6} \times (600) \]
\[ = 1036.4 \text{ Watts} \]

\[ \dot{R} = \frac{1036.4}{0.125} \text{ K/second} \]
\[ = - 8291 \text{ K/second} \]

Theoretical data obtained by applying McAdams equations showed that cooling rates for air, oil and water quenchings are -53.4, -327, and -8291.2°C per second respectively.

The comparison of experimental and theoretical data indicate some degree of accuracy in the investigation.

Evidence to support this claim include Fig. 3.53 which illustrated linear relationship between logarithmic values for both theoretical and experimental data. The aircooling and oil quenching rates data seem to be quite consistent, whereas the water quench data is largely out of trend. Reasons that can be advanced for these observations include assumptions made about physical properties like density, thermal conductivity, thermal capacity and dynamic viscosity, as being constant with temperature.

Errors due to varying thermal properties between the alloy and thermocouple materials can be expected on the experimental side, but presumably, not as significant, as that caused by the theoretical assumptions.

However, these data can only be considered for the tensile specimen geometry under investigation [Fig. 3.48].
THESIS ACCESS FORM

Author: GBADEGESIN JAMES ADETUNJI
Title: MICROSTRUCTURAL CONTROL AND HIGH TEMPERATURE MECHANICAL PROPERTIES OF FERRITIC/MARTENSITIC STEELS FOR NUCLEAR REACTOR APPLICATION

STATUS of access (delete as needed) OPEN / REstricted / CONFIDENTIAL
Moratorium period: ___ years, ending ___ / ___

CONDITIONS of access approved by (capitals): PROF. IAN A MENZIES
DIRECTOR OF RESEARCH (signature): Jan. A. Menzies

DEPARTMENT OF INSTITUTE OF POLYMER TECHNOLOGY AND MATERIALS ENGINEERING

AUTHOR'S DECLARATION: I AGREE THE FOLLOWING CONDITIONS:

OPEN access work shall be made available (in the University and externally) and reproduced as necessary at the discretion of the University Librarian or Head of Department. It may also be copied by the British Library in microfilm or other form for supply to requesting libraries or individuals, subject to an indication of intended use for non-publishing purposes in the following form, placed on the copy and on any covering document or label. The statement itself shall apply to ALL copies:

THIS COPY HAS BEEN SUPPLIED FOR NON-PUBLISHING PURPOSES ON THE UNDERSTANDING THAT IT IS COPYRIGHT MATERIAL AND THAT NO QUOTATION NOR ANY INFORMATION DERIVED FROM THE THESIS MAY APPEAR IN PUBLISHED FORM WITHOUT PRIOR WRITTEN CONSENT BY OR VIA THE UNIVERSITY LIBRARIAN

RESTRICTED / CONFIDENTIAL work: All access and any photocopying shall be strictly subject to written permission from the University Head of Department and external sponsor if any.

AUTHOR'S SIGNATURE [Signature]
DATE 21-9-88

USER'S DECLARATION for signature during any Moratorium period (NOT Open work):
I UNDERTAKE TO UPHOLD THE ABOVE CONDITIONS:

date name (capitals) signature address
Further Work

Informations obtained from various sections of the present study show clearly that further research is required in order to achieve a more comprehensive assessment of high temperature fracture and its relation to microstructure. Below are listed areas of further research suspected can provide more information in addition to those obtained in the present study.

(i) Extensive microstructural investigation of the irradiated samples. Detail study of irradiation induced phases and their role in high temperature process can be appropriate. Analysis of helium bubbles generated during irradiation via \((n,\alpha)\) reactions should be carried out in order to obtain parameters like bubble size, bubble density and bubble spacing. Results from this investigation can be used in explaining low void swelling at high temperatures, and can account for the absence of intergranular mode of fracture.

(ii) Radiation-induced solute segregation should be investigated, notwithstanding the high temperature radiation employed in this work. Alternatively, a lower irradiation temperature can be applied to check the contribution of irradiation temperature and the prior heat treatment.

(iii) The effect of irradiation temperature can be investigated by carrying out irradiation at varied temperature say in the range 400-600°C in steps 50°C. Mechanical property data obtained from this would explain more about irradiation effects. Irradiation dose can also be varied to check if there is a dose correlations to results obtained in the present study.
(iv) Extensive investigation of grain boundary misorientation in ferritic/martensitic steel is very necessary. It was suspected in the present study and from the results obtained that geometrical factors can influence solute element segregation. A little bit of grain boundary energetics' study may be included. Interfacial energies data should also be obtained for 1.4914 steel. Segregation of nickel need to be assessed in more detail in order that a more acceptable explanation can be deduce for its segregation behaviour.

(v) Detail carbide particles analysis should be carried out for the irradiated specimens in order to show the qualitative effect of irradiation on fracture behaviour.

(vi) The combined equilibrium and non-equilibrium model should be extended to include irradiation parameters in order to predict theoretically the extent of segregation occurring during irradiation.

(vii) Charpy impact energy data should be obtained for 1.4914 steels at varied cooling rates and ageing temperatures.
7.0.0.0 Conclusions

1. Fig. 1.9 illustrates schematic isothermal precipitation curves for 1.4914 steel in the temperature range 400-800°C. This represents the summary of phases observed in the present study.

2. During high temperature heat treatment, large MnS, alumina inclusions and primary NbC particles were observed.

3. The fracture mode before and after irradiation is classical cup and cone ductile type for all specimens studied.

4. A linear relationship has been proposed between the reciprocal of the square root of carbide spacing and the mean dimple size.

5. Softer matrix encourages M$_{23}$C$_6$ and NbC particles on lath-lath packet boundaries to act as void initiators by promoting smaller critical particle size for void initiation.

6. Finer dimples have been associated with fine particles; and both have been associated with improved total elongation. Large particles have been associated with premature voidage.

7. Fracture stress is linearly related to the reciprocal of the square root of carbide spacing.
8. Non-equilibrium segregation of silicon and molybdenum to lath and lath packet boundaries has been detected in 12% MoVNb martensitic steel austenitized at 1075°C followed by air, oil and water quenching.

9. Silicon and molybdenum segregation to lath boundaries or particle-matrix interfaces enhances the magnitude of cohesive energy and thereby influence high temperature fracture behaviour. These data has been interpreted using the combination of Ashby and modified Griffith models to explain qualitatively, the influence of silicon and molybdenum segregation. It is also clear that silicon and molybdenum segregation improved fracture toughness.

10. Experimental as well as theoretical cooling rates were determined. Data obtained for the air and oil quenching are not too far out, but that for the water quenching fall out of trend when both theoretical and experimental data are compared. Reasons advanced for the inaccuracies in the theoretical approach are associated with assumptions that physical properties of materials are constant with temperature. However, some degree of accuracy was obtained, indicated by the linear relationship observed for the logarithmic plot of both theoretical and experimental data.

11. FEGSTEM (HB501) is considered a better analytical facility for the determination of solute element segregation than the conventional STEM (JEOL-100CX). This claim has been supported by the outcome of beam spreading calculations and segregation profiles obtained from both systems which indicate a better segregation detection limit (0.032%) for the FEGSTEM against that (1.0%) for the STEM (100CX).
12. Solute segregation has been related to high temperature mechanical behaviour. Ideas of McMahon and Vitek (1979) in combination with those of Ashby (1966) Chen and Knott (1981), and Senior et al (1988) were employed to explain the role of segregants and second phase particles in high temperature ductile fracture.

13. The Hahn and Rosenfield model was applied to show relationship between toughness, flow properties and second phase particle parameters. This relationship indicated strong influence of carbide particles on fracture toughness of ferritic/martensitic steel. Dimple spacing becomes an important parameter to determine failure conditions.

However, the microstructural basis for decohesion in ferritic/martensitic steel has been proposed based on void nucleation at the second phase particles and coalescence; which continued until fracture process is completed.

14. Irradiation at 650°C induced large increase in total elongation and reductions in tensile yield strength.

Helium bubbles have contributed to the high density of dimples observed after irradiation, and hence influence fracture behaviour.

15. Combined irradiation and thermal ageing effects contribute to increasing total elongation and decreasing yield strength.
16. In some samples, larger thermal ageing effects compared to that of irradiation were opposed via some mechanism, suspected, to be radiation hardening to account for large reduction in change of total elongation. It is therefore, possible that radiation hardening mechanism extends to higher irradiation temperatures.

17. Using Ashby equation, values of $d_{\text{crit}}$ were computed as $0.0004\mu m$ and $0.000052\mu m$ for unirradiated, $650^\circ C$, tempered oil quenched samples tested at $500^\circ C$ and $600^\circ C$ respectively. This deduction shows that as we progress through $Q>T>A$ sequence, $d_{\text{crit}}$ decreases.

18. Finally, the present study achieved its aim in relating high temperature mechanical behaviour to microstructural parameters such as solute segregation, carbide particle size, volume fraction, spacing; and dimple size distribution, density and dimple spacing before and after irradiation. Finer carbide particles were associated with finer dimples. Helium bubbles are potential crack nucleators. Combined role of helium bubbles and carbide particles showed large influence on fracture toughness and total elongation.
List of References

4. ADETUNJI, G.J. Paper to be published.
38. BARBU and ARDELL (1975) Scripta Met. 9 1233.
40. BARNES, R.S. and NELSON, R.S. (1965) UKAEA Research group report AERE-R4952.
93. COTTRELL, A.H. (1952) Phil. Mag. 43 645.


107. EDWARD, B.C. et al 81977) BNES Conf. on ferritic steels for fast reactors 22.1-22.5 London 30th May-2nd June.


130a. FRIEDEL, J. (1964) 'Dislocations', Addison Wesley, N.Y.
171. GUIGOT, P. et al (1975) J. de Phys. 36 Colloque c-4 Supple an No. 10 c4-141.


269. KURDJUMOV, G.V. et al (1930) Z. Phys. 64 325.
276. LEMBLE, Ph. (1979) Met. Sc. 13 pp. 496.
301. LOMER, W.M. (1951) Phil. Mag. 42 1327.
346. NORGETT, M.J. (19729 UKAEA, Rept. TP 494.
356. OKAMOTO, P.R. et al (1973) ANS Trans. 16 70.
379. PUTTICK, K.E. (1959) Phil. Mag. 4 964.


List of Figures

1.1 Graph of hardness against tempering temperature for stabilised (1.4914) and unstabilised (1.4923) steels [Heat treatment 1]

1.2 Graph of hardness against cooling rate for unstabilised (1.4923) and stabilised (1.4914) steels [Heat treatment 1]

1.3 Optical micrograph showing martensitic structure and prior austenite grain size

1.4 Thin foil TEM micrograph of quenched materials, showing $M_2X$ needles [Nb.AC.TO]

1.5a Extraction replica of quenched material, showing c-iron carbide, $M_23C_6$ and NbC phases [Nb.AC.TO]

1.5b Thin foil TEM micrograph showing boundary migration in an oil quenched sample tempered at 750°C [Na.OQ.T1]

1.5c Thin foil TEM micrograph of material tempered at higher temperature, 750°C [Na.AC.T1]

1.5d Thin foil TEM micrograph showing slip bands associated with dislocation tangles in substructure [Na.AC.T1]

1.6a Thin foil TEM micrograph showing spheroidal structure with carbide precipitation on lath and prior austenite boundaries

1.6b Thin foil TEM micrograph showing formation of new/subgrain after tempering at 750°C

1.6c Thin foil TEM micrograph showing reduced dislocation density due to higher tempering temperature

1.6d Thin foil TEM micrograph showing microstructure of stabilised alloy temperature at 750°C

1.6e Thin foil TEM micrograph showing formation of new/subgrains due to tempering of unstabilised alloy at 750°C [Ua.AC.T1]
1.7a Thin foil TEM Micrograph showing prior austenite grain boundary and fine M$_2$X needles in a water quenched sample [Nb.AC.TO]

1.7b Thin foil TEM micrograph showing comparable structure of materials tempered at 650°C to the untempered alloy

1.8 Thin foil TEM micrograph showing large primary NbC observed in all specimens before tempering

1.9 Schematic isothermal precipitation curve for 1.4914 steel.

1.10 Extraction replica of material tempered at 750°C showing spherical NbC and more irregular M$_{23}$C$_6$ [Nb.AC.T1]

1.11 Thin foil TEM micrograph showing an isolated rod-shaped structure analysed as NbC (~15nm) in a tempered, oil quenched sample

1.12 Extraction replica of oil quenched material tempered at 650°C showing large spherical NbC and smooth face irregular shaped M$_{23}$C$_6$ [Heat treatment 1]

1.13 Relative dimple sizes as a fraction of fracture surface area for various heat treatments [Heat treatment 1]

1.14a SEM micrograph of fracture surface in a quenched material [Na.AC.TO]

1.14b SEM micrograph of fracture surface in a tempered material [Na.OQ.T1]

1.14c SEM micrograph of fracture surface in a tempered and long term aged material [Na.OQ.T1+5500 hr./590°C]

1.14d SEM micrograph of fracture surface showing a dimple central region and a perimeter of shear [Heat treatment 1]

1.15 Graph of fracture stress against reciprocal of the square root of carbide particle spacing [Heat treatment 1]

1.16a Graph of dimple area mean radius versus the reciprocal of the square root of the interparticle spacing [Heat treatment 1]

1.16b Graph of tempering temperature against carbide volume fraction for aircooled 1.4914 steel tested at at 600°C [Heat treatment 1]
1.17 Carbide particle distribution in oil quenched, long term aged 1.4914 steel tempered at 750°C [Heat treatment 1]

1.18 Relationship of carbide size distribution and tempering temperature for aircooled unirradiated 1.4914 steel tested at 600°C [Heat treatment 1]

1.19 Graph of tempering temperature against inverse of square root of carbide particle spacing in 1.4914 steel [Heat treatment 1]

1.21 Typical histograms showing the proportions of fracture surface area populated by a dimple size range [Heat treatment 1]

1.22 Schematic picture of the fracture surface morphology as a function of heat treatment in 1.4914 steel

1.23 Carbon replica TEM micrograph from etched surface perpendicular to fracture surface in quenched material [Na.OQ.TO]

2.24 Graph showing silicon segregation as a function of cooling rate, ageing time and temperature

2.25 Isometric plots showing relationship of silicon segregation, solution treatment temperature and cooling rate.

2.26 Graph showing molybdenum segregation as a function of cooling rate, ageing time and temperature

2.27 Isometric plots illustrating molybdenum segregation as a function of cooling rate and solution treatment temperature

2.28 Graph showing chromium segregation as a function of ageing time

2.29 Isometric plots illustrating chromium segregation as a function of solution treatment temperature, cooling rate and tempering temperature

2.30 Graphs showing boron segregation as a function of ageing time

2.31 Isometric plots showing boron segregation as a function of cooling rate, solution treatment and tempering temperature
2.32 Graph showing niobium segregation as a function of cooling rate and ageing time

2.33 Isometric plots illustrating niobium segregation as a function of cooling rate and solution treatment temperature

2.34 Graph showing vanadium segregation as a function of ageing time

2.35 Isometric plots illustrating vanadium segregation as a function of cooling rate and solution treatment temperature

2.36a Silicon mean segregation on lath boundaries in untempered 1.4914 steel (HB501 FEGSTEM)

2.36c Molybdenum mean concentration on lath boundaries in untempered 1.4914 steel (HB501 FEGSTEM)

2.36b Graph showing molybdenum mean segregation profiles on lath boundaries in untempered 1.4914 steel (HB501 FEGSTEM)

2.36e Nickel mean segregation profiles on lath boundaries in an untempered 1.4914 steel (HB501 FEGSTEM)

2.37 Graph of solute element mean segregation on lath boundaries against cooling rate for untempered 1.4914 steel (HB501 FEGSTEM)

2.38 Molybdenum mean segregation profiles on lath boundaries in tempered 1.4914 steel (HB501 FEGSTEM)

2.39 Silicon mean segregation profiles on lath boundaries in tempered 1.4914 steel (HB501 FEGSTEM)

2.40 Nickel mean segregation profiles on lath boundaries in tempered 1.4914 steel (HB501 FEGSTEM)

2.41 Graph showing mean silicon segregation profiles obtained from FEGSTEM (HB501) and STEM (100CX) analyses of water quenched 1.4914 steel

2.42 Graph showing mean molybdenum segregation profiles obtained from FEGSTEM (HB501) and STEM (100CX) analyses of water quenched 1.4914 steel

2.43 Graph showing chromium segregation profiles obtained from FEGSTEM (HB501) and STEM (100CX) analyses of water quenched 1.4914 steel
2.44 Sketch of beam spreading on foil surface in STEM (100CX) and FEGSTEM (HB501)

2.45 Graph of fracture energy against cooling rate for 1.4914 steel

2.46 Graph showing relationship of total elongation, cooling rate and solute element segregation in samples tempered at 650°C

2.47 Graph showing relationship of tensile yield strength, cooling rate and solute element segregation in samples tempered at 650°C

3.48 Tensile specimens drawing [Heat treatments I and II]

3.49 Block diagram to show equipment layout for quenching rate determination

3.50 Air cooling curve

3.51 Oil quenching curve

3.52 Water quenching curve

3.53 Logarithmic relationship between the experimental and theoretical cooling rates for 1.4914 steel

3.54 Graph of tensile yield strength against carbide particle size for unirradiated 1.4914 steel [Heat treatment II]

3.55 Effect of tensile test temperature on carbide size distribution in water quenched 1.4914 steel tempered at 650°C

3.56 Graph of carbide particle size against cooling rate for unirradiated 1.4914 steel tempered at 650°C (as treated II condition)

3.57 Carbide size distribution showing effect from cooling rate variation in unirradiated 1.4914 steel (as treated II condition)

3.58 Graph to show carbide particle strengthening in air cooled 1.4914 steel tested at 600°C

3.59 Graph of tensile yield strength against inverse of the square root of carbide spacing in an oil quenched 1.4914 steel tested at 600°C
3.60 Graph of total elongation against carbide volume fraction in aircooled 1.4914 steel tested at 600°C
3.61 Drawing of specimen cartridge assembly used during irradiation
3.62 SEM micrograph of fracture surface showing large inclusion in an oil quenched alloy [Heat treatment 2]
3.63 SEM micrograph of fracture surface showing dimples in an irradiated water quenched alloy tempered at 750°C [Heat treatment 2]
3.64 SEM micrograph of fracture surface showing dimples in an unirradiated alloy with same heat treatment as in Fig. 3.63 but tested at 500°C
3.65 SEM micrograph of fracture surface showing large number of fine dimples in an irradiated alloy tempered at 700°C [Heat treatment 2]
3.66 SEM micrograph of fracture surface showing small number of fine dimples in an unirradiated alloy tempered at 700°C [Heat treatment 2]
3.67 SEM micrograph of fracture surface showing necking features in an irradiated oil quenched alloy fractured at 600°C [Heat treatment 2]
3.68 SEM micrograph of fracture surface showing necking features in unirradiated oil quenched alloy fractured at 600°C [Heat treatment 2]
3.69 SEM micrograph of fracture surface showing dimple distribution in unirradiated alloy at 650°C [Heat treatment 2]
3.70 SEM micrograph of fracture surface showing dimple distribution in unirradiated alloy tempered at 700°C [Heat treatment 2]
3.71 SEM micrograph of fracture surface showing dimple distribution in unirradiated alloy tempered at 750°C [Heat treatment 2]
3.72 SEM micrograph of fracture surface showing small number of small dimples in unirradiated alloy tempered at 650°C [Heat treatment 2]
3.73 SEM micrograph of fracture surface showing small number of large dimples in an irradiated alloy tempered at 650°C [Heat treatment 2]
3.74 SEM micrograph of fracture surface illustrating tearing processes in an air cooled alloy tempered at 650°C [Heat treatment 2]

3.75 SEM micrograph of fracture surface illustrating tearing of water quenched alloy tempered at 750°C [Heat treatment 2]

3.77 Graphs of tensile yield strength against test temperature for 1.4914 steel [Heat treatment II]

3.78 Graphs of tensile yield strength against test temperature for 1.4914 steel [Heat treatment II]

3.79 Graphs of tensile yield strength against cooling rate for 1.4914 steel [Heat treatment II]

3.80 Graphs of tensile yield strength against cooling rate for 1.4914 steel [Heat treatment II]

3.81 Graphs of tensile yield strength against tempering temperature [Heat treatment II]

3.82 Graphs of tensile yield strength against tempering temperature [Heat treatment II]

3.83 Graphs of total elongation against test temperature [Heat treatment II]

3.84 Graphs of total elongation against test temperature [Heat treatment II]

3.85 Graphs of total elongation against tempering temperature [Heat treatment II]

3.86 Graphs of total elongation against tempering temperature [Heat treatment II]

3.87 Graphs of total elongation against cooling rate [Heat treatment II]

3.88 Graphs of total elongation against cooling rate [Heat treatment II]

3.89 Dimple size distribution in oil quenched, 650°C tempered 1.4914 steel tested at 600°C [Heat treatment II]

3.90 Dimple size distribution in water quenched, 750°C tempered 1.4914 steel irradiated at 650°C [Heat treatment II]
3.91 Dimple size distribution in oil quenched, 700°C tempered 1.4914 steel tested at 600°C [Heat treatment II]

3.92 Graph showing mean dimple size distribution in irradiated, 750°C tempered 1.4914 steel tested at 500°C [Heat treatment II]

3.93 Graph of fracture stress against inverse of square root of mean dimple spacing for 1.4914 steel tested at 600°C [Heat treatment II]

3.94 Graph of dimple density against total elongation for 1.4914 steel irradiation at 650°C [Heat treatment II]

3.95 Graph of dimple density against tensile yield strength for 1.4914 steel tested at 600°C [Heat treatment II]

3.96 Graph of mean dimple size against tempering temperature for air cooled, irradiated 1.4914 steel tested at 600°C [Heat treatment II]

3.97 Graph of dimple size against carbide particle size for oil quenched, 650°C tempered 1.4914 steel tested at 600°C [Heat treatment II]

3.98 Graph of dimple size against carbide particle size for irradiated, untempered, waterquenched 1.4914 steel tested at 600°C [Heat treatment II]

3.99 Graph of dimple size against carbide particle size for aircooled, 650°C tempered 1.4914 steel tested at 600°C [Heat treatment II]

3.100 Graph showing hardness against tempering temperature for aircooled unirradiated 1.4914 [Heat treatment II]

3.101 Graph showing hardness against tempering temperature for oil quenched unirradiated 1.4914 [Heat treatment II]

3.102 Graph showing hardness against tempering temperature for water quenched unirradiated 1.4914 steel [Heat treatment II]

3.103 Graph showing hardness against cooling rate in 1.4914 steel tempered at 650°C [Heat treatment II]
Graph showing hardness against cooling rate for unirradiated 1.4914 steel tempered at 750°C
[Heat treatment II]

Graph showing hardness against cooling rate for unirradiated 1.4914 steel tempered at 750°C
[Heat treatment II]

Graph showing relationship of calculated fracture toughness and total elongation
Fig. 1.1
Graph of hardness against tempering temperature for stabilised (1.4914) and unstabilised (1.4923) steels

Legend
- Untempered/unstabilised
- Untempered/stabilised
- Tempered/unstabilised
- Enlarged grain size

Fig. 1.2
Graph of hardness against cooling rate for unstabilised (1.4923) and stabilised (1.4914) steels

Legend
- Unstabilised (1.4923)
- Enlarged Grain size
- Stabilised (1.4914)
- Enlarged Grain size
Fig. 1.3 Optical micrograph showing martensitic structure and prior austenite grain size.
Fig. 1.3(d) Nb.AC.Tl

Fig. 1.4 Thin foil TEM micrograph of quenched material showing $M_2X$ needles [Nb.AC.Tl].

Fig. 1.5a Extraction replica of quenched material, showing $\varepsilon$-iron carbide, $M_{23}C_6$ and NbC phases [Nb.AC.Tl].
Fig. 1.5b Thin foil TEM micrograph showing boundary migration in an oil quenched sample tempered at 750°C [Na,00,Tl].

Fig. 1.5c Thin foil TEM micrograph of material tempered at higher temperature, 750°C [Na,AC,Tl].

Fig. 1.5d Thin foil TEM micrograph showing slip bands associated with dislocation tangles in substructure [Na,AC,Tl].
Fig. 1.6a Thin foil TEM micrograph showing spheroidal structure with carbide precipitation on lath and prior austenite boundaries.

Fig. 1.6b Thin foil TEM micrograph showing formation of new/subgrain after tempering at 750°C.

Fig. 1.6c Thin foil TEM micrograph showing reduced dislocation density due to higher tempering temperature.
Fig. 1.6d Thin foil TEM micrograph showing microstructure of stabilised alloy tempered at 750°C.

Fig. 1.6e Thin foil TEM micrograph showing formation of new/subgrains due to tempering of unstabilised alloy at 750°C [Nb.AC.T1].

Fig. 1.7a Thin foil TEM micrograph showing prior austenite grain boundary and fine M_X needles in a water quenched sample [Nb.AC.T0].
Fig. 1.7b Thin foil TEM micrograph showing comparable structure of materials tempered at 650°C to the untempered alloy.

Fig. 1.8 Thin foil TEM micrograph showing large primary NbC observed in all specimens before tempering.
Fig. 1.9 Schematic Isothermal Precipitation Curve for 1.4914
Fig. 1.10 Extraction replica of material tempered at 750°C showing spherical NbC and more irregular $M_{23}C_6$ [Nb,AC,Tl].

Fig. 1.11 Thin foil TEM micrograph showing an isolated rod shaped structure analysed as NbC (~1.5μm) in a tempered, oil quenched sample.

Fig. 1.12 Extraction replica STEM micrograph showing smooth face NbC and $M_{23}C_6$ particles in oil quenched samples tempered at 650°C.
LONG TERM AGE PLUS CREEP

<table>
<thead>
<tr>
<th></th>
<th>Na. 00.T1</th>
<th>7</th>
<th>14</th>
<th>12</th>
<th>6</th>
<th>11</th>
<th>9</th>
<th>6</th>
<th>15</th>
<th>6</th>
<th>9</th>
<th>5</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
</table>

LONG TERM AGE

<table>
<thead>
<tr>
<th></th>
<th>Na. 00.T4</th>
<th>47</th>
<th>23</th>
<th>6</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.</td>
<td>Na. 00.T1</td>
<td>30</td>
<td>30</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

TEMPERED

<table>
<thead>
<tr>
<th></th>
<th>Na. AC.T1</th>
<th>16</th>
<th>27</th>
<th>24</th>
<th>16</th>
<th>9</th>
<th>3</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.</td>
<td>Na. AC.T2</td>
<td>15</td>
<td>24</td>
<td>18</td>
<td>16</td>
<td>9</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>29.</td>
<td>Na. AC.T3</td>
<td>16</td>
<td>27</td>
<td>21</td>
<td>20</td>
<td>6</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>10.</td>
<td>Na. 00.T1</td>
<td>20</td>
<td>33</td>
<td>21</td>
<td>20</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>4.</td>
<td>Nb. AC.T1</td>
<td>6</td>
<td>24</td>
<td>30</td>
<td>24</td>
<td>9</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

QUENCHED MARTEMISITE

<table>
<thead>
<tr>
<th></th>
<th>Na. IQ.T0</th>
<th>9</th>
<th>30</th>
<th>24</th>
<th>12</th>
<th>13</th>
<th>9</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.</td>
<td>Na. AC.T0</td>
<td>9</td>
<td>27</td>
<td>21</td>
<td>15</td>
<td>9</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>8.</td>
<td>Na. 00.T0</td>
<td>9</td>
<td>21</td>
<td>21</td>
<td>9</td>
<td>9</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>14.</td>
<td>Na. WQ.T0</td>
<td>12</td>
<td>27</td>
<td>21</td>
<td>9</td>
<td>7</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>5.</td>
<td>Nb. AC.T0</td>
<td>9</td>
<td>36</td>
<td>21</td>
<td>12</td>
<td>9</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 1.13 Relative dimple sizes as a fraction of fracture surface area for various heat treatments
Fig. 1.14a SEM micrograph of fracture surface in a quenched material [Na.AC.IO].

Fig. 1.14b SEM micrograph of fracture surface in a tempered material [Na.AC.TI].

Fig. 1.14c SEM micrograph of fracture surface in a tempered and long term aged material [Na.OQ.T]+5500hr.590c].
Fig. 1.14d SEM micrograph of fracture surface showing a simple central region and perimeter of shear [Heat treatment 1].
Fig. 1.15 Graph of fracture stress against reciprocal of the square root of the interparticle spacing (Heat treatment 1)
Fig. 1.16a Graph of dimple area mean radius versus the reciprocal of the square root of the interparticle spacing (Heat temperature 1)
Fig. 1.16b
Graph of tempering temperature against carbide volume fraction for aircooled 1.4914 steel tested at 600 C (heat treatment 1)

Fig. 1.17
Carbide particle distribution in oil quenched, long term aged 1.4914 steel tempered at 750 C (Heat treatment 1)

Fig. 1.18
Relationship of carbide size distribution and tempering temperature for aircooled unirradiated 1.4914 steel tested at 600 C (Heat treatment 1)
Fig. 1.19
Graph of tempering temperature against inverse of sq. root of carbide particle spacing in 1.4914 steel [Heat treatment 1]
Fig. 1.21 Typical Histograms showing the proportions of fracture surface area populated by a dimple size range.

[Heat treatment 1]

(a) 21 Na.AC.TO  
Area mean = 2.52 \( \mu m \) (4.60)  
H\(_V\) = 361

(b) 26 Na.AC.T1  
Area mean = 2.35 \( \mu m \) (4.21)  
H\(_V\) = 238
(c) 20. Ua.AC.TO
area mean = 1.84 μm (6.32)
$H_v = 397$

(d) 23. Ua.AC.T1
area mean = 1.16 μm (2.53)
$H_v = 269$
Fig. 1.22 Schematic picture of the fracture surface morphology as a function of heat treatment in 1.4914

**QUENCHED: HARD MATRIX;**
\[ d_{crit} \text{ large} \]

**TEMPERED: MEDIUM SOFT MATRIX;**
\[ d_{crit} \text{ medium} \]

**LONG TERM AGE: SOFT MATRIX;**
\[ d_{crit} \text{ small} \]
Fig. 1.23 Carbon replica TEM micrograph from etched surface perpendicular to fracture surface in quenched material [Na.AC.T0].
Fig. 2.28

- 220 -

Cr in 1.4914 (A.C., 600°C)

aggregation intensity

Cr in 1.4914 (H.C., 600°C)

aggregation intensity

Cr in 1.4914 (H.C., 600°C)

aggregation intensity

Cr in 1.4914 (H.C., 600°C)

aggregation intensity
Cr segregation model in 1.4914 (Untempered)

Fig. 2.29
Fig. 2.30

**Segregation Intensity**

B in 14914 (50.600°C)

---

**Segregation Intensity**

B in 14914 (50.600°C)
Fig. 2.31

\textbf{g segregation model 1.4914 (Untempered)}

![Diagram of g segregation model at 650°C](image1)

![Diagram of g segregation model at 700°C](image2)

![Diagram of g segregation model at 750°C](image3)
Fig. 2.32

 Nb in 1.4914 (00.600C)

 Nb in 1.4914 (00.600C)
Fig. 2.33 Nb segregation model in 1.4914 (Untempered)

- Nb segregation model in 1.4914 Tempered at 520°C
- Nb segregation model in 1.4914 Tempered at 700°C
Fig. 2.34
Fig. 2.35a

Segregation model in 1.4914 (Untempered)

Segregation model in 1.4914 (Tempered at 650°C)

Segregation model in 1.4914 (Tempered at 700°C)

Segregation model in 1.4914 (Tempered at 720°C)
Fig. 2.35b Thin foil TEM micrograph showing lath boundary in an oil quenched sample exhibiting strong silicon and molybdenum segregation.
Fig. 2.36a
Mean silicon segregation profile on lath boundaries in 1.4914 steel at varied cooling rate

Fig. 2.36b
Silicon mean segregation on lath boundaries in untempered 1.4914 steel (HB501 FEGSTEM)
Fig. 2.36c
Molybdenum mean concentration on lath boundaries in untempered 1.4914 steel

- Cooling rate (°C/sec.)
- Molybdenum segregation (wt%)

Fig. 2.36d
Graph showing molybdenum mean segregation profiles on lath boundaries in untempered 1.4914 steel (HB S01 FEGSTEM)

- Dist. from lath boundary (nm)
- Molybdenum (wt%)

Fig. 2.36e
Nickel mean segregation profiles on lath boundaries in an untempered 1.4914 steel (HB501 FEGSTEM)

- Dist. from lath boundary (nm)
- Nickel segregation (wt%)
**Fig. 2.37**
Graph of solute element mean segregation on lath boundaries against cooling rate for untempered 1.4914 steel (HB501 FEGSTEM).

![Graph of solute element mean segregation on lath boundaries against cooling rate for untempered 1.4914 steel (HB501 FEGSTEM)](image)

**Legend**
- △ Silicon
- × Si ref. level
- □ Molybdenum
- ○ Mo ref. level
- □ Nickel
- × Ni ref. level
- ✦ Vanadium
- ★ V ref. level

**Fig. 2.38**
Molybdenum mean segregation profile on lath boundaries in tempered 1.4914 steel (VG HB501 FEGSTEMMA).

![Molybdenum mean segregation profile on lath boundaries in tempered 1.4914 steel (VG HB501 FEGSTEMMA)](image)

**Legend**
- △ 650 °C TEMPO
- × 700 °C TEMPE
- □ 750 °C TEMPE
- ☉ REFERENCE
Fig. 2.39  
Silicon mean segregation profile on lath boundaries in tempered 1.4914 steel (VG HB501 FEGSTEMMA)

Fig. 2.40  
Nickel mean segregation profile on lath boundaries in 1.4914 steel (VG HB501 FEGSTEMMA)
Fig. 2.41 Graph showing mean silicon segregation profile obtained from FEGSTEMMA(HB501) and STEMMA(JEOL-100CX) analyses of water quenched 1.4914 steel.

Fig. 2.42 Graph showing mean molybdenum segregation profile obtained from FEGSTEMMA(HB501) and STEMMA(JEOL-100CX) analyses of water quenched 1.4914 steel.
Graph showing chromium segregation profile obtained from FEGSTEMMA (HB501) and STEMMA (JEOL-100CX) analyses of water quenched 1.4914 steel.

Figure 2.44 Sketch of beam spreading on foil surface in STEM (100CX) and FEGSTEM (HB501)

---

Legend

- STEM (100CX)
- FEGSTEM (HB501)

---

- Impurity boundary layer limits (thickness = 20Å)
- X-ray source boundary limits
Fig. 2.45  Graph of fracture energy against cooling rate for 1.4914 steel [Heat treatment 1].

After L. Schaefer (1986)
Graph showing relationship of total Elongation, Cooling rate and solute element segregation in samples tempered.

Fig. 2.47

Graph showing relationship of tensile yield strength, cooling rate and solute element segregation in samples tempered.
Fig. 3.48A Tensile specimen drawing [Heat treatment 1]

Fig. 3.48b Tensile specimen drawing [Heat treatment II]
Fig. 3.49 Block diagram to show equipment layout for quenching rate determination
Fig. 3.50  Graph showing the air cooling curve
Fig. 3.51  Graph showing the oil quenching curve
Fig. 3.52 Graph showing the water quenching curve
Fig. 3.53
Logarithmic relationship between the experimental and theoretical cooling rates for 1.4914 steel

![Graph of the logarithmic relationship between experimental and theoretical cooling rates for 1.4914 steel.]

Fig. 3.54
Graph of tensile yield strength against carbide particle size for unirradiated 1.4914 steel [Heat treatment II]

![Graph of tensile yield strength against carbide particle size.]

Fig. 3.55
Effect of tensile test temperature on carbide size distribution in water quenched 1.4914 steel tempered at 650°C

![Graph showing the effect of tensile test temperature on carbide size distribution.]
Fig. 3.56 Graph of carbide particle size against cooling rate for unirradiated 1.4914 steel tempered at 650°C (as treated condition)

Fig. 3.57 Carbide size distribution showing effect from cooling rate variation in unirradiated 1.4914 steel (as treated condition)

Fig. 3.58 Graph to show carbide particle strengthening in air cooled 1.4914 steel tested at 600°C

*Sample lists on table 1.2
Fig. 3.59
Graph of tensile yield strength against inverse of the sq.root of carbide spacing in an oil quenched 1.4914 steel tested at 600 C

- 244 -

Fig. 3.60
Graph of total elongation against carbide volume fraction in aircooled 1.4914 steel tested at 600 C

*Sample list in table 3.18

*Sample list in table 1.2
Fig. 3.61 Drawing of specimen cartridge assembly used during irradiation.

Fig. 3.62 SEM micrograph of fracture surface showing large inclusion in an oil quenched alloy [Heat treatment 2].

Fig. 3.63 SEM micrograph of fracture surface showing dimples in an irradiated water quenched alloy tempered at 750°C [Heat treatment 2].
Fig. 3.64 SEM micrograph of fracture surface showing dimples in an unirradiated alloy with some heat treatment as in Fig. 3.63 but tested at 500°C.

Fig. 3.65 SEM micrograph of fracture surface showing large number of fine dimples in an irradiated alloy tempered at 700°C [Heat treatment 2].

Fig. 3.66 SEM micrograph of fracture surface showing small number of fine dimples in an unirradiated alloy tempered at 700°C [Heat treatment 2].
Fig. 3.67 SEM micrograph of fracture surface showing necking features in an irradiated oil quenched alloy fracture at 600°C [Heat treatment 2].

Fig. 3.68 SEM micrograph of fracture surface showing necking features in unirradiated oil quenched alloy fractured at 600°C [Heat treatment 2].
Fig. 3.69 SEM micrograph of fracture surface showing dimple distribution of unirradiated alloy tempered at 650°C [Heat treatment 2].

Fig. 3.70 SEM micrograph of fracture surface showing dimple distribution in unirradiated alloy tempered at 700°C [Heat treatment 2].

Fig. 3.71 SEM micrograph of fracture surface showing dimple distribution in unirradiated alloy tempered at 750°C [Heat treatment 2].
Fig. 3.72 SEM micrograph of fracture surface showing small number of small dimples in an unirradiated alloy tempered at 650°C [Heat treatment 2].

Fig. 3.73 SEM micrograph of fracture surface showing small number of large dimples in an irradiated alloy tempered at 650°C [Heat treatment 2].
Fig. 3.74 SEM micrograph of fracture surface illustrating tearing processing in an air cooled alloy tempered at 650°C (Heat treatment 2).

(a) irradiated

(b) unirradiated
Fig. 3.75 SEM micrograph of fracture surface illustrating tearing on side wall of water quenched alloy tempered at 750°C [Heat treatment 2].

(a) irradiated

(b) unirradiated
Fig. 3.77

(a) Graph of tensile yield strength against test temperature for 650°C tempered and irradiated 1.4914 steel quenched in air.

(b) Graph of tensile yield strength against test temperature for 700°C tempered and irradiated 1.4914 steel quenched in air.

(c) Graph of tensile yield strength against test temperature for 750°C tempered and irradiated 1.4914 steel quenched in air.

Graph of tensile yield strength against test temperature for 650°C tempered and irradiated 1.4914 steel quenched in oil.

Graph of tensile yield strength against test temperature for 700°C tempered and irradiated 1.4914 steel quenched in oil.

Graph of tensile yield strength against test temperature for 750°C tempered and irradiated 1.4914 steel quenched in oil.
Fig. 3.78

(a) 

Graph of tensile yield strength against test temperature for 650 °C tempered and irradiated 1.4914 steel quenched in water.

(b) 

Graph of tensile yield strength against test temperature for 700 °C tempered and irradiated 1.4914 steel quenched in water.

(c) 

Graph of tensile yield strength against test temperature for 750 °C tempered and irradiated 1.4914 steel quenched in water.
Fig. 3.79

(a) Graph of tensile yield strength against cooling rate for 650°C tempered, irradiated 14914 steel tested at 500°C

(b) Graph of tensile yield strength against cooling rate for 700°C tempered and irradiated 14914 steel tested at 500°C

(c) Graph of tensile yield strength against cooling rate for 750°C tempered, irradiated 14914 steel tested at 500°C
Fig. 3. (a) Graph of tensile yield strength against cooling rate for 650 C tempered, irradiated 1.4914 steel tested at 650 C.

(b) Graph of tensile yield strength against cooling rate for 700 C tempered, irradiated 1.4914 steel tested at 650 C.

(c) Graph of tensile yield strength against cooling rate for 750 C tempered, irradiated 1.4914 steel tested at 650 C.
Fig. 3.81

(a) Graph of tensile yield strength against tempering temperature for 500°C test of irradiated 1.4914 steel quenched in air.

(b) Graph of tensile yield strength against tempering temperature for 600°C test of irradiated 1.4914 steel quenched in air.

(c) Graph of tensile yield strength against tempering temperature for 650°C test of irradiated 1.4914 steel quenched in air.
Graph of tensile yield strength against tempering temperature
for 500°C test of irradiated 1.4914 steel quenched in water

Legend
- measured
- extrapolated

Graph of tensile yield strength against tempering temperature
for water quenched, irradiated 1.4914 steel tested at 600°C

Legend
- measured
- extrapolated

Graph of tensile yield strength against tempering temperature
for 650°C test of irradiated 1.4914 steel quenched in water

Legend
- measured
- extrapolated
Fig. 3.83

(a) Graph of total elongation against test temperature for oil quenched, irradiated 1.4914 steel tempered at 650 C

(b) Graph of total elongation against test temperature for oil quenched, irradiated 1.4914 steel tempered at 700 C

(c) Graph of total elongation against test temperature for oil quenched, irradiated 1.4914 steel tempered at 750 C
Graph of total elongation against test temperature for 650°C tempered, irradiated 1.4914 steel quenched in water.

Graph of total elongation against test temperature for water quenched, irradiated 1.4914 steel tempered at 700°C.

Graph of total elongation against test temperature for water quenched, irradiated 1.4914 steel tempered at 750°C.
Fig. 3.85

(a) Graph of total elongation against tempering temperature for 500 C test of irradiated 14914 steel quenched in air

(b) Graph of total elongation against tempering temperature for 500 C test of irradiated 14914 steel quenched in oil

(c) Graph of total elongation against tempering temperature for 600 C test of irradiated 14914 steel quenched in air

(d) Graph of total elongation against tempering temperature for 600 C test of irradiated 14914 steel quenched in oil

(e) Graph of total elongation against tempering temperature for 650 C test of irradiated 14914 steel quenched in air

(f) Graph of total elongation against tempering temperature for 650 C test of irradiated 14914 steel quenched in oil
Fig. 3.86

(a) Graph of total elongation against tempering temperature for 500 C test of irradiated 1.4914 steel quenched in water

(b) Graph of total elongation against tempering temperature for 600 C test of irradiated 1.4914 steel quenched in water

(c) Graph of total elongation against tempering temperature for 650 C test of irradiated 1.4914 steel quenched in water
Fig. 3.87

(a) Graph of total elongation against cooling rate for 650°C tempered, irradiated 1.4914 steel tested at 500°C

(b) Graph of total elongation against cooling rate for 650°C tempered, irradiated 1.4914 steel tested at 600°C

(c) Graph of total elongation against cooling rate for 650°C tempered, irradiated 1.4914 steel tested at 650°C

Legend:
- IRROJ.
- IAOI.
- UPO.

Graph of total elongation against cooling rate for 500°C test of irradiated 1.4914 steel tempered at 700°C

Legend:
- IRROJ.
- IAOI.
- UPO.

Cooling rate (deg.C/sec.)
Graph of total elongation against cooling rate for 750°C tempered, irradiated 1.4914 steel tested at 500°C

Legend
- Irradiated
- Unirradiated

Cooling rate (deg.C/sec.)

Graph of total elongation against cooling rate for 750°C tempered, irradiated 1.4914 steel tested at 600°C

Legend
- Irradiated
- Unirradiated

Cooling rate (deg.C/sec.)

Graph of total elongation against cooling rate for 750°C tempered, irradiated 1.4914 steel tested at 650°C

Legend
- Irradiated
- Unirradiated

Cooling rate (deg.C/sec.)
Fig. 3.89
Dimple size distribution in oil quenched, 650°C tempered 1.4914 steel tested at 600°C

[Heat treatment II]

Fig. 3.90
Dimple size distribution in water quenched, 750°C tempered 1.4914 steel irradiated at 650°C
Fig. 3.91
Dimple size distribution in oil quenched, 700°C tempered 1.4914 steel tested at 600°C

Legend
- UNIRRADIATED
- IRRADIATED

Fig. 3.92
Graph showing mean dimple size distribution in unirradiated, 750°C tempered 1.4914 steel tested at 500°C

Legend
- AIRCOOLED
- OIL QUENCHED
- WATER QUENCHED
Fig. 3.93
Graph of fracture stress against inverse of square root of mean dimple spacing for 1.4914 steel tested at 600°C

Legend
- IRRADIATED
- UNIRRADIATED

Sample list in table 3.18
** Sample list in table 3.19

Fig. 3.94
Graph of dimple density against total elongation for 1.4914 steel irradiated at 650°C

Legend
- IRRADIATED
- UNIRRADIATED

Sample list in
** table 3.19
* table 3.18
Fig. 3.95
Graph of dimple density against tensile yield strength for 1.4914 steel tested at 600 C

Graph of mean dimple size against tempering temperature for aircooled 1.4914 steel tested at 600 C
Fig. 3.97
Graph of dimple size against carbide particle size for oil quenched, 650°C tempered 1.4914 steel tested at 600°C.

Legend
- IRRADIATED
- UNIRRADIATED

Fig. 3.98
Graph of dimple size against carbide particle size for irradiated, untempered water quenched 1.4914 steel tested at 600°C.
Fig. 3.99
Graph of dimple size against carbide particle size for aircool, 650 C tempered 1.4914 steel tested at 600 C

Legend
- IRRADIATED
- UNIRRADIATED

Carbide particle size (microns)

Fig. 3.100
Graph showing hardness against tempering temperature for aircooled unirradiated 1.4914 steel

Legend
- AGED
- NOT AGED

Tempering temperature (deg.C)
Fig. 3.101
Graph showing hardness against tempering temperature for oil quenched unirradiated 1.4914 steel

Legend
- AGED
- NOT AGED

Fig. 3.102
Graph showing hardness against tempering temperature for water quenched unirradiated 1.4914 steel

Legend
- AGED
- NOT AGED
Fig. 3.103  
Graph showing hardness against cooling rate in 1.4914 steel tempered at 650°C

Fig. 3.104  
Graph showing hardness against cooling rate for unirradiated 1.4914 steel tempered at 700°C
Fig. 3.105
Graph showing hardness against cooling rate for unirradiated 1.4914 steel tempered at 750°C

Legend
- Acid
- Not acid

Fig. 3.106 Graph of fracture toughness (K_Ic) against total elongation for 1.4914 steel tested at 600°C [Heat treatment 2]

Legend
- IRRADIATED
- UNIRRADIATED
List of Tables

1.1 Chemical composition of ferritic/martensitic steels
1.2 Mechanical property data [Heat treatment 1]
1.3 Statistical analysis of carbide particles in 1.4914 and 1.4923 steels [Heat treatment 1]
1.4a Volume fraction of carbide particles in relation to fracture stress for aircooled 1.4914 steel [Heat treatment 1]
1.4b Fracture stress in relation to the inverse of the square root of carbide particle spacing in 1.4914 steel [Heat treatment 1]
1.5a Characterised carbide particles [Heat treatment 1]
1.5b Analysed of secondary NbC particles on lath boundaries [Heat treatment 1]
2.6a Relationship of solute segregation, cooling rate and total elongation in an untempered 1.4914 steel tested at 600°C
2.6b Relationship of solute segregation, cooling rate and tensile yield strength in an untempered 1.4914 steel tested at 600°C
2.7a Mean solute segregation on lath boundaries at varied cooling rates in 1.4914 steel [HB501] FEGSTEM
2.7b Mean silicon segregation profiles on lath boundaries in 1.4914 steel [FEGSTEM (HB5019]
2.7c Number of lath boundaries analysed for silicon and molybdenum segregation
2.8 Comparative mean segregation data obtained from the FEGSTEM (HB501) and STEM (JEOL-100CX) analyses of selected lath boundaries in a water quenched 1.4914 steel.
2.9 Characteristics of FEGSTEM (HB501) and STEM (100CX)
3.10a Relationship of carbide spacing and yield strength for oil quenched 1.4914 steel tested at 600°C [Heat treatment II]

3.10b Relationship of volume fraction and total elongation in 650°C tempered 1.4914 steel tested at 500°C [Heat treatment II]

3.11 Statistical data of carbide particles in as treated 1.4914 steel [Heat treatment II]

3.12 Heat treatment II conditions employed for irradiated samples

3.13 Flux Monitors: Cross sections and half-lives

3.14 Irradiation parameters

3.15a Tensile data for water quenched and irradiated 1.4914 steel tested at 500°C [Heat treatment II]

3.15b Tensile data for water quenched and irradiated 1.4914 steel tested at 600°C

3.15c Tensile data for water quenched and irradiated 1.4914 steel tested at 650°C

3.16a Tensile data for oil quenched and irradiated 1.4914 steel tested at 500°C [Heat treatment II]

3.16b Tensile data for oil quenched and irradiated 1.4914 steel tested at 600°C

3.16c Tensile data for oil quenched and irradiated 1.4914 steel tested at 650°C

3.17a Tensile data for aircooled and irradiated 1.4914 steel tested at 500°C [Heat treatment II]

3.17b Tensile data for aircooled and irradiated 1.4914 steel tested at 600°C

3.17c Tensile data for aircooled and irradiated 1.4914 steel tested at 650°C

3.18 Tensile test data for unirradiated 1.4914 steel [Heat treatment II]

3.19 Tensile test data for irradiated 1.4914 steel [Heat treatment II]
3.20  Dimple size distribution for 1.4914 steel [Heat treatment II]

3.21  Statistical data of dimples in irradiated 1.4914 steel [Heat treatment II]

3.22  Statistical data of dimples in unirradiated 1.4914 steel [Heat treatment II]

3.23  Statistical data of carbide particles in 1.4914 steel after fracture [Heat treatment II]

3.24  Vickers hardness test data for aged and non-aged 1.4914 steel [Heat treatment II]

3.25  Fracture toughness data for unirradiated 1.4914 steel [Heat treatment II]

3.26  Fracture toughness data for irradiated 1.4914 steel [Heat treatment II]
Table 1.1  Chemical composition of ferritic/martensitic steel

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Nb</th>
<th>B</th>
<th>N</th>
<th>C</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4914</td>
<td>0.45</td>
<td>0.35</td>
<td>11.3</td>
<td>0.7</td>
<td>0.5</td>
<td>0.3</td>
<td>0.25</td>
<td>70 ppm</td>
<td>0.029</td>
<td>0.11</td>
<td>Bal.</td>
</tr>
<tr>
<td>1.4923</td>
<td>0.37</td>
<td>0.5</td>
<td>11.2</td>
<td>0.42</td>
<td>0.83</td>
<td>0.21</td>
<td>-</td>
<td>1 ppm</td>
<td>0.01</td>
<td>0.21</td>
<td>Bal.</td>
</tr>
<tr>
<td>Sample No.</td>
<td>Stability</td>
<td>SCLn Therm.</td>
<td>Cooling Rate</td>
<td>Tempering Temp.</td>
<td>Vickers Hardness</td>
<td>Brinell Hardness</td>
<td>Strained Time to Fracture min</td>
<td>Elongation (approx)</td>
<td>Fracture Surface</td>
<td>Mean Grain Prior</td>
<td>Dimple Mean Radius</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>-------------</td>
<td>--------------</td>
<td>-----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>--------------------------</td>
<td>---------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>2</td>
<td>U</td>
<td>b</td>
<td>AC</td>
<td>T0 400</td>
<td>537</td>
<td></td>
<td>14:08</td>
<td>24</td>
<td></td>
<td></td>
<td>161</td>
</tr>
<tr>
<td>3</td>
<td>U</td>
<td>b</td>
<td>AC</td>
<td>T1 268</td>
<td>299</td>
<td></td>
<td>14:28</td>
<td>36</td>
<td></td>
<td></td>
<td>161</td>
</tr>
<tr>
<td>4</td>
<td>N</td>
<td>b</td>
<td>AC</td>
<td>T1 238</td>
<td>261</td>
<td></td>
<td>11:44</td>
<td>28</td>
<td>0.73</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>N</td>
<td>a'</td>
<td>CQ</td>
<td>T0 369</td>
<td>466</td>
<td></td>
<td>11:32</td>
<td>23</td>
<td>0.93</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>N</td>
<td>a'</td>
<td>CQ</td>
<td>T0 362</td>
<td>466</td>
<td></td>
<td>13:10</td>
<td>25</td>
<td>0.90</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>N</td>
<td>a'</td>
<td>CQ</td>
<td>T0 405</td>
<td>537</td>
<td></td>
<td>13:27</td>
<td>22</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>10</td>
<td>N</td>
<td>a'</td>
<td>CQ</td>
<td>T1 238</td>
<td>259</td>
<td></td>
<td>9:35</td>
<td>32</td>
<td>0.75</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>11</td>
<td>N</td>
<td>a'</td>
<td>CQ</td>
<td>T1 268</td>
<td>376</td>
<td></td>
<td>11:40</td>
<td>34</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>13</td>
<td>U</td>
<td>a</td>
<td>WQ</td>
<td>T0 392</td>
<td>410</td>
<td></td>
<td>8:48</td>
<td>2</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>14</td>
<td>N</td>
<td>a</td>
<td>WQ</td>
<td>T0 365</td>
<td>500</td>
<td></td>
<td>12:11</td>
<td>22</td>
<td>1.00</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>15</td>
<td>U</td>
<td>a</td>
<td>OQ</td>
<td>T0 408</td>
<td>448</td>
<td></td>
<td>15:02</td>
<td>23</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>17</td>
<td>N</td>
<td>a</td>
<td>OQ</td>
<td>T0 365</td>
<td>500</td>
<td></td>
<td>11:56</td>
<td>21</td>
<td>0.87</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>18</td>
<td>U</td>
<td>a</td>
<td>OQ</td>
<td>T0 414</td>
<td>448</td>
<td></td>
<td>12:58</td>
<td>27</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>19</td>
<td>N</td>
<td>a</td>
<td>OQ</td>
<td>T0 360</td>
<td>537</td>
<td></td>
<td>11:58</td>
<td>20</td>
<td>1.00</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>20</td>
<td>U</td>
<td>a</td>
<td>AC</td>
<td>T0 397</td>
<td>448</td>
<td></td>
<td>10:45</td>
<td>-</td>
<td>0.90</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>21</td>
<td>N</td>
<td>a</td>
<td>AC</td>
<td>T0 361</td>
<td>486</td>
<td></td>
<td>11:25</td>
<td>-</td>
<td>0.90</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>22</td>
<td>U</td>
<td>a</td>
<td>AC</td>
<td>T0 351</td>
<td>537</td>
<td></td>
<td>8:52</td>
<td>20</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>23</td>
<td>U</td>
<td>a</td>
<td>AC</td>
<td>T1 269</td>
<td>410</td>
<td></td>
<td>0:05</td>
<td>26</td>
<td>0.90</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>25</td>
<td>N</td>
<td>a</td>
<td>AC</td>
<td>T1 238</td>
<td>261</td>
<td></td>
<td>9:45</td>
<td>31</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>26</td>
<td>N</td>
<td>a</td>
<td>AC</td>
<td>T1 238</td>
<td>261</td>
<td></td>
<td>8:45</td>
<td>39</td>
<td>0.59</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>27</td>
<td>U</td>
<td>a</td>
<td>AC</td>
<td>T3 319</td>
<td>336</td>
<td></td>
<td>13:30</td>
<td>34</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>28</td>
<td>N</td>
<td>a</td>
<td>AC</td>
<td>T3 257</td>
<td>299</td>
<td></td>
<td>9:32</td>
<td>36</td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>29</td>
<td>N</td>
<td>a</td>
<td>AC</td>
<td>T3 267</td>
<td>336</td>
<td></td>
<td>12:50</td>
<td>29</td>
<td>0.77</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>30</td>
<td>U</td>
<td>a</td>
<td>AC</td>
<td>T2 299</td>
<td>336</td>
<td></td>
<td>13:12</td>
<td>34</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>31</td>
<td>N</td>
<td>a</td>
<td>AC</td>
<td>T2 253</td>
<td>299</td>
<td></td>
<td>9:40</td>
<td>24</td>
<td>0.77</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>33</td>
<td>U</td>
<td>a</td>
<td>AC</td>
<td>T0 397</td>
<td>410</td>
<td></td>
<td>50:00</td>
<td>24</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>34</td>
<td>U</td>
<td>a</td>
<td>OQ</td>
<td>T1 265</td>
<td>299</td>
<td></td>
<td>16:20</td>
<td>29</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>35</td>
<td>U</td>
<td>a</td>
<td>OQ</td>
<td>T1 270</td>
<td>299</td>
<td></td>
<td>19:00</td>
<td>29</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>36</td>
<td>N</td>
<td>a</td>
<td>OQ</td>
<td>T4 301</td>
<td></td>
<td></td>
<td>26</td>
<td></td>
<td>0.66</td>
<td></td>
<td>206</td>
</tr>
<tr>
<td>37</td>
<td>N</td>
<td>a</td>
<td>OQ</td>
<td>T1 275</td>
<td></td>
<td></td>
<td>26</td>
<td></td>
<td>1.07</td>
<td></td>
<td>2.88</td>
</tr>
<tr>
<td>38</td>
<td>N</td>
<td>a</td>
<td>OQ</td>
<td>T1 275</td>
<td>160</td>
<td>4381hhrs</td>
<td>26</td>
<td></td>
<td>2.00</td>
<td></td>
<td>7.67</td>
</tr>
</tbody>
</table>

**Key:**
- U = Unstabilised
- N = Nb Stabilised
- b = 2h @ 1250°C 5h @ 1075°C
- a = 1h @ 1075°C
- a' = a performed twice

**Cooling rates from 1075°C**
- WQ = Water Quench
- OQ = Oil Quench
- AC = Air Cool
- ID = Interrupted Quench (air cooled to 400°C-maintained for 24 h)

**Tempering at:**
- 1h Tempering Applied
- T1 = 750°C
- T2 = 700°C
- T3 = 650°C
- T4 = 600°C

*Note: Temperature values and time points are approximate.*
Table 1.3 Statistical Analysis of Carbide Particles in 1.4914 and 1.4723 Steels [Heat Treatment 1]

<table>
<thead>
<tr>
<th>Sample Nos.</th>
<th>Mean temperature (°C)</th>
<th>Fracture stress (MPa)</th>
<th>Volume fraction of carbide particles</th>
<th>Critical particle diameter (approx)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>460</td>
<td>486</td>
<td>0.177</td>
<td>8.4 x 10^{-6}</td>
</tr>
<tr>
<td>29</td>
<td>650</td>
<td>336</td>
<td>0.149</td>
<td>4.4 x 10^{-6}</td>
</tr>
<tr>
<td>31</td>
<td>700</td>
<td>299</td>
<td>0.121</td>
<td>9.8 x 10^{-6}</td>
</tr>
<tr>
<td>4</td>
<td>750</td>
<td>261</td>
<td>0.098</td>
<td>6.2 x 10^{-6}</td>
</tr>
</tbody>
</table>

Table 1.4a Volume fraction of carbide particles in relation to fracture stress for aircooled 1.4914 steel [Heat Treatment 1]

<table>
<thead>
<tr>
<th>Sample Nos.</th>
<th>Mean temperature (°C)</th>
<th>Fracture stress (MPa)</th>
<th>Volume fraction of carbide particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>460</td>
<td>486</td>
<td>0.177</td>
</tr>
<tr>
<td>29</td>
<td>650</td>
<td>336</td>
<td>0.149</td>
</tr>
<tr>
<td>31</td>
<td>700</td>
<td>299</td>
<td>0.121</td>
</tr>
<tr>
<td>4</td>
<td>750</td>
<td>261</td>
<td>0.098</td>
</tr>
</tbody>
</table>

Table 1.4b Fracture stress in relation to the inverse of the square root of inter carbide particle spacing for 1.4914 steel [Heat Treatment 1]

<table>
<thead>
<tr>
<th>Sample Nos.</th>
<th>Vickers hardness (HV)</th>
<th>Critical particle diameter (μm)</th>
<th>Fracture stress (MPa)</th>
<th>Volume fraction of carbide particles</th>
<th>Critical particle diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>261</td>
<td>1.26</td>
<td>8.4 x 10^{-6}</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>486</td>
<td>2.37</td>
<td>4.4 x 10^{-6}</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>448</td>
<td>2.67</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>486</td>
<td>1.96</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>410</td>
<td>1.49</td>
<td>9.79 x 10^{-6}</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>261</td>
<td>1.94</td>
<td>4.7 x 10^{-6}</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>336</td>
<td>2.05</td>
<td>4.6 x 10^{-6}</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>299</td>
<td>1.66</td>
<td>6.2 x 10^{-6}</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.5a  Characterised Carbide Particles [Heat treatment 1]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total No. of particles examined</th>
<th>Secondary NbC</th>
<th>Secondary CrC</th>
<th>%NbC</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>701</td>
<td>130</td>
<td>571</td>
<td>18.5</td>
</tr>
<tr>
<td>5</td>
<td>215</td>
<td>15</td>
<td>200</td>
<td>6.9</td>
</tr>
<tr>
<td>21</td>
<td>124</td>
<td>5</td>
<td>119</td>
<td>4</td>
</tr>
<tr>
<td>26</td>
<td>602</td>
<td>43</td>
<td>559</td>
<td>7</td>
</tr>
<tr>
<td>29</td>
<td>338</td>
<td>20</td>
<td>318</td>
<td>5.9</td>
</tr>
<tr>
<td>31</td>
<td>307</td>
<td>28</td>
<td>279</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 1.5b  Analysis of Secondary NbC particles on lath boundaries [Heat treatment 1]

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X$ (µm)</th>
<th>$Y$ (µm)</th>
<th>f</th>
<th>$\sigma_F$</th>
<th>$H_v$</th>
<th>$\frac{1}{\lambda}$</th>
<th>Tempering Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3.2</td>
<td>0.07</td>
<td>0.0116</td>
<td>261</td>
<td>228</td>
<td>0.56</td>
<td>750</td>
</tr>
<tr>
<td>5</td>
<td>1.93</td>
<td>0.01</td>
<td>0.009</td>
<td>486</td>
<td>369</td>
<td>0.72</td>
<td>600</td>
</tr>
<tr>
<td>21</td>
<td>1.73</td>
<td>0.02</td>
<td>0.0054</td>
<td>486</td>
<td>361</td>
<td>0.76</td>
<td>600</td>
</tr>
<tr>
<td>26</td>
<td>1.84</td>
<td>0.045</td>
<td>0.18</td>
<td>261</td>
<td>230</td>
<td>0.74</td>
<td>750</td>
</tr>
<tr>
<td>31</td>
<td>2.4</td>
<td>0.028</td>
<td>0.015</td>
<td>299</td>
<td>253</td>
<td>0.65</td>
<td>700</td>
</tr>
<tr>
<td>29</td>
<td>1.6</td>
<td>0.058</td>
<td>0.025</td>
<td>366</td>
<td>267</td>
<td>0.79</td>
<td>650</td>
</tr>
<tr>
<td>37</td>
<td>1.47</td>
<td>0.054</td>
<td>0.026</td>
<td>–</td>
<td>275</td>
<td>0.62</td>
<td>750</td>
</tr>
</tbody>
</table>
Table 2.6a  Relationship of Solute Segregation, Cooling rate and total Elongation in an untempered 1.4914 steel tested at 600°C

<table>
<thead>
<tr>
<th>Cooling rate °C/sec</th>
<th>AC (6.5)</th>
<th>OQ (50)</th>
<th>WQ (220)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Elongation (%)</td>
<td>4</td>
<td>5.9</td>
<td>5.17</td>
</tr>
<tr>
<td>Silicon segregation (wt %)</td>
<td>0.57</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Molybdenum Segregation (wt %)</td>
<td>0.88</td>
<td>1.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2.6b  Relationship of Solute Segregation, Cooling rate and tensile yield strength in an untempered 1.4914 steel tested at 600°C

<table>
<thead>
<tr>
<th>Cooling rate °C/sec</th>
<th>AC (6.5)</th>
<th>OQ (50)</th>
<th>WQ (220)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>227.8</td>
<td>222.2</td>
<td>132</td>
</tr>
<tr>
<td>Silicon segregation (wt %)</td>
<td>0.57</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Molybdenum segregation (wt %)</td>
<td>0.88</td>
<td>1.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2.7a  Mean solute segregation on both boundaries at varied cooling rates in 1.4914 steel [FEGSTEM (H850)]

<table>
<thead>
<tr>
<th>Cooling rate °C/sec</th>
<th>Silicon (wt%)</th>
<th>Molybdenum (wt%)</th>
<th>Nickel (wt%)</th>
<th>Vanadium (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC 6.5</td>
<td>0.57</td>
<td>0.88</td>
<td>0.92</td>
<td>0.26</td>
</tr>
<tr>
<td>OQ 50</td>
<td>1.4</td>
<td>1.1</td>
<td>0.95</td>
<td>0.25</td>
</tr>
<tr>
<td>WQ 220</td>
<td>0.7</td>
<td>0.1</td>
<td>1.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 2.7b  Mean silicon segregation profiles on both boundaries in 1.4914 steel [HB501 FEGSTEMMA]

<table>
<thead>
<tr>
<th>Distance from both boundary (µm)</th>
<th>WQ 220 °C/sec</th>
<th>OQ 50 °C/sec</th>
<th>AC 6.5 °C/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.7</td>
<td>3.6</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
<td>0.7</td>
<td>1.3</td>
<td>0.6</td>
</tr>
<tr>
<td>10</td>
<td>0.6</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>15</td>
<td>0.5</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>20</td>
<td>0.6</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>30</td>
<td>0.6</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>50</td>
<td>0.6</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>100</td>
<td>0.6</td>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>200</td>
<td>3.3</td>
<td>1.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2.7c  Number of both boundaries analysed for silicon and Molybdenum segregation

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Total No. of both boundary examined</th>
<th>No. of both boundaries showing silicon and Molybdenum segregation</th>
<th>No. of both boundaries showing no segregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC 6.5°/sec</td>
<td>300</td>
<td>110</td>
<td>190</td>
</tr>
<tr>
<td>OQ</td>
<td>300</td>
<td>50</td>
<td>250</td>
</tr>
<tr>
<td>50°C/sec</td>
<td>300</td>
<td>230</td>
<td>70</td>
</tr>
<tr>
<td>WQ 220°C/sec</td>
<td>300</td>
<td>230</td>
<td>70</td>
</tr>
</tbody>
</table>
Table 2.8 Comparative mean segregation data obtained from the FEGSTEMMA (VG HB501) and STEMMA (JEOL-100CX) analyses of selected lath boundaries in a water quenched 1.4914 steel.

<table>
<thead>
<tr>
<th>Distance from lath boundary (μm)</th>
<th>Silicon (wt%)</th>
<th>Molybdenum (wt%)</th>
<th>Nickel (wt%)</th>
<th>Chromium (wt%)</th>
<th>Vanadium (wt%)</th>
<th>Manganese (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB501 JEOL 100CX</td>
<td>0.61</td>
<td>1.86</td>
<td>0.8</td>
<td>10.3</td>
<td>11.55*</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>0.51*</td>
<td>0.53*</td>
<td>0.82*</td>
<td>12.05</td>
<td>0.34*</td>
<td>0.66</td>
</tr>
<tr>
<td>5</td>
<td>0.79</td>
<td>0.76</td>
<td></td>
<td>10.16</td>
<td>11.75*</td>
<td>0.16</td>
</tr>
<tr>
<td>10</td>
<td>0.53</td>
<td>0.50</td>
<td>0.87</td>
<td>10.3</td>
<td>0.25</td>
<td>0.6</td>
</tr>
<tr>
<td>15</td>
<td>0.55</td>
<td>0.89</td>
<td></td>
<td>10.3</td>
<td>0.23</td>
<td>0.63</td>
</tr>
<tr>
<td>20</td>
<td>0.56</td>
<td>1.1</td>
<td>0.83</td>
<td>10.26</td>
<td>11.49*</td>
<td>0.23</td>
</tr>
<tr>
<td>25</td>
<td>0.52</td>
<td>0.35</td>
<td>0.84</td>
<td>10.3</td>
<td>0.17</td>
<td>0.56</td>
</tr>
<tr>
<td>30</td>
<td>0.45</td>
<td>0.42</td>
<td></td>
<td>12.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>0.46</td>
<td>0.54</td>
<td></td>
<td>11.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.9 Characteristics of FEGSTEM (HB501) and STEM (100CX).

<table>
<thead>
<tr>
<th></th>
<th>FEGSTEM (HB501)</th>
<th>STEM (JEOL 100CX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam source</td>
<td>Thermal field emission</td>
<td>Tungsten</td>
</tr>
<tr>
<td>Beam brightness</td>
<td>(10^{13} \text{Am}^{-2} \text{Sr}^{-1})</td>
<td>(3 \times 10^9 \text{Am}^{-2} \text{Sr}^{-1})</td>
</tr>
<tr>
<td>Beam stability</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td>Source size</td>
<td>5nm</td>
<td>50μm</td>
</tr>
<tr>
<td>Energy spread</td>
<td>0.5 - 2eV</td>
<td>2 - 3eV</td>
</tr>
<tr>
<td>Probe size</td>
<td>&lt; 1nm</td>
<td>2 - 20nm</td>
</tr>
<tr>
<td>Coherency</td>
<td>higher degree</td>
<td>lower degree</td>
</tr>
<tr>
<td>Beam current</td>
<td>In A</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.10a Relationship of carbide spacing and yield strength for oil quenched 1.4914 steel tested at 600°C [Heat treatment II]

<table>
<thead>
<tr>
<th>$\frac{1}{\lambda}$ (μm$^{-1}$)</th>
<th>$\sigma_y$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>222</td>
</tr>
<tr>
<td>0.34</td>
<td>91.5</td>
</tr>
<tr>
<td>0.49</td>
<td>240</td>
</tr>
</tbody>
</table>

Table 3.10b Relationship of volume fraction and total elongation in 650°C tempered 1.4914 steel tested at 500°C [Heat Treatment II]

<table>
<thead>
<tr>
<th>Volume fraction</th>
<th>Total Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>4</td>
</tr>
<tr>
<td>0.002</td>
<td>4.8</td>
</tr>
<tr>
<td>0.076</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3.11 Statistical data of carbide particles in as treated 1.4914 steel [Heat treatment II + no tensile test]

<table>
<thead>
<tr>
<th>Samples</th>
<th>f</th>
<th>$\bar{d}$ (μm)</th>
<th>$\bar{X}$ (μm)</th>
<th>$\frac{1}{v} (μm^3)$</th>
<th>p</th>
<th>$\frac{\alpha \times 10^{12}}{m^{-2}}$</th>
<th>Tempering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OQ</td>
<td>.047</td>
<td>.396</td>
<td>6.4</td>
<td>.39</td>
<td>120</td>
<td>9.7467</td>
<td>$T_0$</td>
</tr>
<tr>
<td>WQ</td>
<td>.23</td>
<td>.49</td>
<td>1.99</td>
<td>.71</td>
<td>397</td>
<td>6.4108</td>
<td>$T_0$</td>
</tr>
<tr>
<td>AC</td>
<td>.012</td>
<td>.22</td>
<td>26.4</td>
<td>.19</td>
<td>214</td>
<td>35.6715</td>
<td>$T_1$</td>
</tr>
<tr>
<td>OQ</td>
<td>.013</td>
<td>.11</td>
<td>7.3</td>
<td>.37</td>
<td>123</td>
<td>3302.96</td>
<td>$T_1$</td>
</tr>
<tr>
<td>WQ</td>
<td>.05</td>
<td>.048</td>
<td>.87</td>
<td>1.1</td>
<td>641</td>
<td>646.73</td>
<td>$T_1$</td>
</tr>
<tr>
<td>AC</td>
<td>.136</td>
<td>.05</td>
<td>1.55</td>
<td>.8</td>
<td>721.5</td>
<td>689.9</td>
<td>$T_2$</td>
</tr>
<tr>
<td>WQ</td>
<td>.35</td>
<td>.34</td>
<td>4.0</td>
<td>.5</td>
<td>635</td>
<td>0.907</td>
<td>$T_2$</td>
</tr>
<tr>
<td>CQ</td>
<td>.005</td>
<td>.025</td>
<td>4.2</td>
<td>.49</td>
<td>54</td>
<td>2096.88</td>
<td>$T_2$</td>
</tr>
<tr>
<td>AC</td>
<td>.019</td>
<td>.16</td>
<td>9.4</td>
<td>.33</td>
<td>80</td>
<td>26.4</td>
<td>$T_1$</td>
</tr>
<tr>
<td>CQ</td>
<td>.39</td>
<td>.86</td>
<td>4.9</td>
<td>.45</td>
<td>76</td>
<td>0.43</td>
<td>$T_1$</td>
</tr>
<tr>
<td>WQ</td>
<td>.104</td>
<td>.302</td>
<td>5.6</td>
<td>.42</td>
<td>163</td>
<td>3.6</td>
<td>$T_1$</td>
</tr>
</tbody>
</table>

f = Vol. fraction
$\bar{d}$ = mean particle diameter
$\bar{X}$ = mean interparticle spacing
p = number of particles analysed
$\alpha$ = carbide particle density
Table 3.12  Heat treatment II conditions employed for irradiated samples

Aircool
+ 650°C temper
+ 700°C temper
+ 750°C temper

Oil Quench
+ 650°C temper
+ 700°C temper
+ 750°C temper

Water Quench
+ 650°C temper
+ 700°C temper
+ 750°C temper

Table 3.13  Flux Monitors: cross sections and half-lives

<table>
<thead>
<tr>
<th>Monitor</th>
<th>Reaction</th>
<th>Cross Section</th>
<th>Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>Co(^{59}) (n,\gamma) Co(^{60})</td>
<td>58* barns</td>
<td>5-27 years</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni(^{58}) (n,\alpha) Co(^{59}) Co(^{59}) (n,\gamma) Co(^{59})</td>
<td>107.7m barns</td>
<td>71.5 days</td>
</tr>
<tr>
<td></td>
<td>Co(^{58}) (n,\gamma) Co(^{59})</td>
<td>1.8x10(^5) barns</td>
<td>Co(^{59}) = 9hrs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1730 barns</td>
<td></td>
</tr>
</tbody>
</table>

* 1 barn = 10\(^{-24}\) cm

Table 3.14  Irradiation parameters

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Thermal Dose (n.cm^{-2})</th>
<th>Fission Dose (n.cm^{-2})</th>
<th>Damage (dpa) (Fe,NRT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>3.478 \times 10(^{20})</td>
<td>1.011 \times 10(^{20})</td>
<td>0.154</td>
</tr>
<tr>
<td>Middle</td>
<td>3.478 \times 10(^{20})</td>
<td>1.231 \times 10(^{20})</td>
<td>0.188</td>
</tr>
<tr>
<td>Bottom</td>
<td>3.478 \times 10(^{20})</td>
<td>1.117 \times 10(^{20})</td>
<td>0.170</td>
</tr>
</tbody>
</table>

Fission Dose rate = 3.35 - 6.52 \times 10\(^{-13}\) n.cm\(^{-2}\).sec\(^{-1}\)

Flux Characteristics:
- 0.014% > 10MeV; 6.67% > 1MeV
- 14.87% > 0.1MeV; spectrum averaged neutron energy = 0.226 MeV

Table 3.15a  Tensile data for water quenched and irradiated 1.4914 steel tested at 500°C [Heat treatment II]

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>Tensile yield strength (MPa)</th>
<th>Total Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>261.5, 12.6*</td>
<td>71.8*</td>
</tr>
<tr>
<td>700</td>
<td>239.5, 33.3*</td>
<td>121, 71.8*</td>
</tr>
<tr>
<td>750</td>
<td>121, 71.8*</td>
<td>7.7, 7.7*</td>
</tr>
</tbody>
</table>

Table 3.15b  Tensile data for water quenched and irradiated 1.4914 steel tested at 600°C [Heat treatment II]

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>Tensile yield strength (MPa)</th>
<th>Total Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>114.0, 90.4*</td>
<td>46.9*</td>
</tr>
<tr>
<td>700</td>
<td>90.5, 42.8*</td>
<td>112, 46.9*</td>
</tr>
<tr>
<td>750</td>
<td>6, 17.8*</td>
<td>6, 17.8*</td>
</tr>
</tbody>
</table>

* Irradiated
Table 3.15c  Tensile data for water quenched and irradiated 1.4914 steel tested at 650°C [Heat treatment II]

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>111.6, 30*</td>
<td>55.5, 20.5*</td>
<td>112.5, 35*</td>
</tr>
<tr>
<td>Total elongation (%)</td>
<td>8.8, 16.5*</td>
<td>3.9, 16.5*</td>
<td>4.6, 15.4*</td>
</tr>
</tbody>
</table>

*Irradiated:

Table 3.16a  Tensile data for oil quenched and Irradiated 1.4914 steel tested at 500°C [Heat treatment II]

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>398, 24.7*</td>
<td>189, 41.5*</td>
<td>168.7, 42.8*</td>
</tr>
<tr>
<td>Total elongation (%)</td>
<td>4.8, 8.5*</td>
<td>4, 7.5*</td>
<td>6.8, 8.0*</td>
</tr>
</tbody>
</table>

Table 3.16b  Tensile data for oil quenched and Irradiated 1.4914 steel tested at 600°C [Heat treatment II]

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>91.5, 58.3*</td>
<td>239.9, 75.4*</td>
<td>253.7, 61.4*</td>
</tr>
<tr>
<td>Total elongation (%)</td>
<td>6, 13.97*</td>
<td>5.8, 13.4*</td>
<td>7.5, 13.9*</td>
</tr>
</tbody>
</table>

Table 3.16c  Tensile data for oil quenched and Irradiated 1.4914 steel tested at 650°C [Heat treatment II]

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>105.5, 65.6*</td>
<td>159.5, 12.5*</td>
<td>86, 28*</td>
</tr>
<tr>
<td>Total elongation (%)</td>
<td>4.2, 15.9*</td>
<td>4.2, 17.5*</td>
<td>7.1, 12.8*</td>
</tr>
</tbody>
</table>

Table 3.17a  Tensile data for aircooled and irradiated 1.4914 steel tested at 500°C [Heat treatment II]

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>168.2, 50.2*</td>
<td>184.2, 26.8*</td>
<td>178, 69.2*</td>
</tr>
<tr>
<td>Total elongation (%)</td>
<td>4, 9.2*</td>
<td>5.7, 7.45*</td>
<td>3, 8.88*</td>
</tr>
</tbody>
</table>

Table 3.17b  Tensile data for aircooled and irradiated 1.4914 steel tested at 600°C

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>208, 35.6*</td>
<td>142.2, 103.8*</td>
<td>119.7, 109.7*</td>
</tr>
<tr>
<td>Total elongation (%)</td>
<td>3.4, 16.3*</td>
<td>4.6, 8.18*</td>
<td>7, 16.9*</td>
</tr>
</tbody>
</table>

Table 3.17c  Tensile data for aircooled and irradiated 1.4914 steel tested at 650°C

<table>
<thead>
<tr>
<th>Tempering temp. (°C)</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile yield strength (MPa)</td>
<td>134.8, 125.4*</td>
<td>127.5, 106.9*</td>
<td>93, 14*</td>
</tr>
<tr>
<td>Total elongation (%)</td>
<td>3.6, 19.4*</td>
<td>4.7, 16.9*</td>
<td>6, 11.4*</td>
</tr>
</tbody>
</table>

*Irradiated
285
Table 3.18

Tensile test data for unirrodioted 1.4914 steel [Heat treatment UJ

E
E

.
~

Q.

u

•
~

E

d.
E

!

!

z
""

E

z•

c

"

1

47

1.5

603.2

168.2

368.2

596.2

13586

1.13

liS
346
47

1.64

666.7

398

414.7

400.7

20090

1.165

1.49

613.5

261.5

39S.5

521.5

14510

0.66

2

1.39

562.2

184.2

363.2

55S.2

11304

1.44

5.7

5.6
6.8
2.6
27.9

liS
346
47
liS
346
47

1.33

542

189

388

533

11458

4

29.6

1.38
1.3
1.26
1.19

566.5
521
503.7
480

2)9.5
178
168.7
121

37S.5
360
315.7
314

295.5
261
24S.7
92

22167
18736

1.05
1.07

3.9

3.3

3
6.8

1.01

391

308

302

276

11969

7.1
26.7
25.9
3.9
27.6
26.8
28.6
26.5
1.9
21.9

7
DO 8
AC

WO

9

AC 1D
DO 11
WO 12
AC 13
DO 14
WO 15
AC 16

DQ 17
WO 18
AC 19

OD 20
WO 21
AC 22

oa

23

WO 24
AC 25
DO 26
WO 27
AC 28

DO 29
WO 30

1.13
1.DJ

442.5
412.2

91.5
114

215.5
218.2

315.5
404.2

6678
14674

1.02

370

142.2

192

249

20944

liS
346
47

0.95

379.9

239.9

208.9

360.9

20861

0.9
D.89

359
363.7

90.5
119.7

D.8)

333.7

0.80
0.83
0.81

318
329.8
323.5

253.7
112

0.85
o. 76

344
307

0.75

liS
?46
47
115
346
47
liS
346
47
liS
346

t mean :, 23679 MNm- 2

7.7
3.4
6

5.3
4.6

201
812
19143
197.7 352.7 20774
162.7
176

1.93
1.55

7.5

192

21964
11117

307.8
316.5

24695
24348

0.99
1.111

3.6
4.2

25.8
3.6
14.5
16.7

111.6 163
127.5 153

272

295

18500
217176

1.03
1.21

301

159.5

166

259

18882

1.14

3.5
4.7
4.2

8.8
20.9
7.0

0.74
0.60
0.65

312.)
276
25S

22879

1.07

3.9

3.3

265
242
241

21566

1. 57

6

19901

1.87

251

171
135
123
119

303.3

0.63

55.3
93
86
11.2

17741

1.25

1.52

579.2

227.8

309.3

108.5

7109,6

0.975

7.1
4.6
4.0

27.4
26.0
28.7

1.5
1.43

515.9
494

222.2
132

210.4
221.6

447.6
488

13051
13830

1.395
1.215

·cmean

134.8 158.8
105.5 162.5

= 9107.3 MNm- 2

321.7

(obtained)

=

oa =
wa =

: 650°C
\

;.a
3.85
7

6

tspecific

569
635.5
503.5
762
589
570
437
915
1061
527
852
910
683
911
430
90D.5

838.2
918.7
831.5
761.2

B7.4fl

669.5
606.2
584

22.72

68. 1(,

22.58
22.4

68.7

550.9
517
529.7

22.7
22.26

63 .Bi~

22.92

72.!1!

995

504.7

23.14

69.41

80~

460

22.76

86.4'7

510.5

500.8
484.5

22.2

7i.8

22.35

75.9!l

525
462
436
453.6
417
387
383

22.24

82.2i

22.42
22.35
22.29
22.77
23.08

n.a;

22.46

67.37

5.86

5.17

1040

MNm-

2

696

757.5
682
691.7

646
480

848.9
821.4

767

(Cottrell (1967)]

!hr tempering at

A0

Tl

:

750°C

Af

= original area
= final area

oilquench

r2

=

7oooc

L

= original gauge length

waterquench

TJ

:

650°C

l

= final

T

= 600°C

Fastest

0

0

gauge length

L

= 21.21 mm

A
0

= 89.82

0

84.89

83.91

21.87
22.65
22.26
22.28
22.01
22.93
2).09
22.14

593.5
545.5
636
600.5
549
813.5
970.5
697.5
775
1188

= 26500

22.34
22.375

aircool

Coollng rate from lOBQOC
AC

= 500°C

r 8 ' 600'1:
Ty

1.72
1.88
D.93
1.51

4

4.8

1.37
1.19
1.49
1.055
1. 71

Tensile test temperature

T0

158~0

7148

liS
346
47

115
346
47

0.87

c

"'

..'::

DO 2
WO 3
DO 5
WO 6

8,
,

c

•"',

,!

4

E
u

8.

AC

~

~

·e"'
AC

c

•

•

mm'

67.9';
66.711
86.89
83.64

68.79
69.2i'

86.3<;.

67.4i

8a.nn

83.74

86.80
6e. JJ
69.211


<table>
<thead>
<tr>
<th>Sample label</th>
<th>Sample number</th>
<th>Cooling rate (°C/sec)</th>
<th>Tempering temp. (°C)</th>
<th>Tensile testing temp. (°C)</th>
<th>Max. tensile stress (MPa)</th>
<th>Tensile yield stress (MPa)</th>
<th>Tensile breaking stress (MPa)</th>
<th>0.2% proof stress (MPa)</th>
<th>Gauge length extension (%</th>
<th>Total elongation (%)</th>
<th>Time to fracture (sec)</th>
<th>Net fracture stress (MPa)</th>
<th>Helium bubble radius (μm)</th>
<th>Void swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1</td>
<td>47</td>
<td>T₁</td>
<td>T₀</td>
<td>375.6</td>
<td>50.2</td>
<td>250.9</td>
<td>345.3</td>
<td>2.04</td>
<td>9.2</td>
<td>1210.5</td>
<td>500.3</td>
<td>.016</td>
<td>11.6-4</td>
</tr>
<tr>
<td>DQ</td>
<td>2</td>
<td>115</td>
<td>T₁</td>
<td>T₀</td>
<td>386.7</td>
<td>24.7</td>
<td>182.2</td>
<td>286.9</td>
<td>1.89</td>
<td>8.5</td>
<td>1126.5</td>
<td>591.2</td>
<td>.014</td>
<td>5.4E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>3</td>
<td>346</td>
<td>T₁</td>
<td>T₀</td>
<td>392.3</td>
<td>12.6</td>
<td>208.5</td>
<td>176.1</td>
<td>2.14</td>
<td>9.6</td>
<td>1294.5</td>
<td>576.1</td>
<td>.014</td>
<td>5.4E-4</td>
</tr>
<tr>
<td>AC</td>
<td>4</td>
<td>42</td>
<td>T₂</td>
<td>T₀</td>
<td>406.1</td>
<td>26.8</td>
<td>235</td>
<td>391.5</td>
<td>1.64</td>
<td>7.45</td>
<td>973</td>
<td>577.2</td>
<td>.014</td>
<td>5.4E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>5</td>
<td>115</td>
<td>T₂</td>
<td>T₀</td>
<td>388.4</td>
<td>41.5</td>
<td>165</td>
<td>361.9</td>
<td>1.66</td>
<td>7.5</td>
<td>988.5</td>
<td>611.8</td>
<td>.013</td>
<td>4.5E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>6</td>
<td>346</td>
<td>T₂</td>
<td>T₀</td>
<td>384.5</td>
<td>33.3</td>
<td>271.6</td>
<td>389.8</td>
<td>2.02</td>
<td>9.1</td>
<td>1197.5</td>
<td>497.4</td>
<td>.016</td>
<td>11.6E-4</td>
</tr>
<tr>
<td>AC</td>
<td>7</td>
<td>47</td>
<td>T₁</td>
<td>T₀</td>
<td>389.4</td>
<td>69.2</td>
<td>237.4</td>
<td>374.4</td>
<td>1.97</td>
<td>8.89</td>
<td>1180.4</td>
<td>541.4</td>
<td>.019</td>
<td>8.6E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>8</td>
<td>115</td>
<td>T₁</td>
<td>T₀</td>
<td>382.5</td>
<td>42.8</td>
<td>256.7</td>
<td>360.3</td>
<td>1.96</td>
<td>8.8</td>
<td>1175.5</td>
<td>508.3</td>
<td>.016</td>
<td>11.6E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>9</td>
<td>346</td>
<td>T₁</td>
<td>T₀</td>
<td>322.6</td>
<td>71.0</td>
<td>177.5</td>
<td>-</td>
<td>1.61</td>
<td>7.3</td>
<td>1926</td>
<td>667.7</td>
<td>.017</td>
<td>15.2E-4</td>
</tr>
<tr>
<td>AC</td>
<td>10</td>
<td>47</td>
<td>T₁</td>
<td>T₀</td>
<td>259.9</td>
<td>35.6</td>
<td>110.8</td>
<td>231.3</td>
<td>3.76</td>
<td>16.3</td>
<td>2668</td>
<td>409</td>
<td>.019</td>
<td>24.9E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>11</td>
<td>115</td>
<td>T₁</td>
<td>T₀</td>
<td>274.4</td>
<td>58.3</td>
<td>113.2</td>
<td>143.9</td>
<td>3.18</td>
<td>15.97</td>
<td>1837</td>
<td>435.6</td>
<td>.018</td>
<td>19.6E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>12</td>
<td>346</td>
<td>T₁</td>
<td>T₀</td>
<td>242.6</td>
<td>90.4</td>
<td>92.7</td>
<td>77.9</td>
<td>2.76</td>
<td>12.2</td>
<td>1586.5</td>
<td>392.5</td>
<td>.02</td>
<td>32.5E-4</td>
</tr>
<tr>
<td>AC</td>
<td>13</td>
<td>47</td>
<td>T₁</td>
<td>T₀</td>
<td>259.6</td>
<td>103.8</td>
<td>117.7</td>
<td>259.9</td>
<td>1.81</td>
<td>8.10</td>
<td>963.5</td>
<td>481.5</td>
<td>.017</td>
<td>15.2E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>14</td>
<td>115</td>
<td>T₁</td>
<td>T₀</td>
<td>278.3</td>
<td>75.4</td>
<td>117.6</td>
<td>103.2</td>
<td>3.04</td>
<td>13.34</td>
<td>1766</td>
<td>439</td>
<td>.018</td>
<td>19.6E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>15</td>
<td>346</td>
<td>T₁</td>
<td>T₀</td>
<td>279.2</td>
<td>42.8</td>
<td>104.6</td>
<td>204.7</td>
<td>3.39</td>
<td>14.18</td>
<td>1971.5</td>
<td>453.8</td>
<td>.018</td>
<td>19.6E-4</td>
</tr>
<tr>
<td>AC</td>
<td>16</td>
<td>47</td>
<td>T₁</td>
<td>T₀</td>
<td>330.6</td>
<td>109.7</td>
<td>146.9</td>
<td>320.7</td>
<td>3.4</td>
<td>14.86</td>
<td>1962.5</td>
<td>530.3</td>
<td>.015</td>
<td>8.6E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>17</td>
<td>115</td>
<td>T₁</td>
<td>T₀</td>
<td>276.8</td>
<td>61.4</td>
<td>109.4</td>
<td>68</td>
<td>3.17</td>
<td>13.9</td>
<td>1893</td>
<td>444.2</td>
<td>.018</td>
<td>39.6E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>18</td>
<td>346</td>
<td>T₁</td>
<td>T₀</td>
<td>277.3</td>
<td>46.9</td>
<td>209.2</td>
<td>155.4</td>
<td>4.13</td>
<td>17.79</td>
<td>2400.5</td>
<td>449.4</td>
<td>.018</td>
<td>39.6E-4</td>
</tr>
<tr>
<td>AC</td>
<td>19</td>
<td>47</td>
<td>T₁</td>
<td>T₀</td>
<td>180.5</td>
<td>125.4</td>
<td>55.2</td>
<td>132.2</td>
<td>4.53</td>
<td>19.35</td>
<td>2740</td>
<td>321.8</td>
<td>.025</td>
<td>8.6E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>20</td>
<td>115</td>
<td>T₁</td>
<td>T₀</td>
<td>185.7</td>
<td>45.4</td>
<td>61</td>
<td>164.1</td>
<td>3.65</td>
<td>15.97</td>
<td>2237.5</td>
<td>306.4</td>
<td>.026</td>
<td>100E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>21</td>
<td>346</td>
<td>T₁</td>
<td>T₀</td>
<td>168.3</td>
<td>30</td>
<td>38.5</td>
<td>2.9</td>
<td>3.8</td>
<td>16.48</td>
<td>2266</td>
<td>298.1</td>
<td>.027</td>
<td>122E-4</td>
</tr>
<tr>
<td>AC</td>
<td>22</td>
<td>47</td>
<td>T₂</td>
<td>T₀</td>
<td>246.4</td>
<td>106.9</td>
<td>88.8</td>
<td>142.6</td>
<td>3.9</td>
<td>16.87</td>
<td>1289.5</td>
<td>404</td>
<td>.019</td>
<td>24.9E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>23</td>
<td>115</td>
<td>T₂</td>
<td>T₀</td>
<td>213.8</td>
<td>12.5</td>
<td>77.1</td>
<td>104.6</td>
<td>4.06</td>
<td>17.5</td>
<td>2394</td>
<td>350.5</td>
<td>.022</td>
<td>48.6E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>24</td>
<td>346</td>
<td>T₂</td>
<td>T₀</td>
<td>196.9</td>
<td>20.5</td>
<td>65.1</td>
<td>182.7</td>
<td>3.8</td>
<td>16.48</td>
<td>2236</td>
<td>328.7</td>
<td>.024</td>
<td>72E-4</td>
</tr>
<tr>
<td>AC</td>
<td>25</td>
<td>47</td>
<td>T₁</td>
<td>T₀</td>
<td>195.4</td>
<td>14</td>
<td>70.6</td>
<td>86.4</td>
<td>2.55</td>
<td>11.13</td>
<td>1513</td>
<td>210.2</td>
<td>.025</td>
<td>86E-4</td>
</tr>
<tr>
<td>DQ</td>
<td>26</td>
<td>115</td>
<td>T₁</td>
<td>T₀</td>
<td>195.4</td>
<td>28</td>
<td>66.7</td>
<td>168</td>
<td>2.9</td>
<td>12.8</td>
<td>1720.5</td>
<td>324.1</td>
<td>.025</td>
<td>86E-4</td>
</tr>
<tr>
<td>WQ</td>
<td>27</td>
<td>346</td>
<td>T₁</td>
<td>T₀</td>
<td>189.9</td>
<td>35</td>
<td>63.5</td>
<td>156.6</td>
<td>3.52</td>
<td>15.4</td>
<td>2091</td>
<td>316.3</td>
<td>.025</td>
<td>86E-4</td>
</tr>
</tbody>
</table>
Table 3.20 Dimple size distribution for 1.4914 steel [Heat treatment I]

Unirradiated

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d=0$</th>
<th>$d=0.05$</th>
<th>$d=0.1$</th>
<th>$d=0.2$</th>
<th>$d=0.3$</th>
<th>$d=0.4$</th>
<th>$d=0.5$</th>
<th>$d=0.6$</th>
<th>$d=0.7$</th>
<th>$d=0.8$</th>
<th>$d=0.9$</th>
<th>$d=1.0$</th>
<th>$d=1.1$</th>
<th>$d=1.2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC $T_1$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>43</td>
<td>51</td>
<td>27</td>
<td>19</td>
<td>21</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OQ $T_1$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>37</td>
<td>25</td>
<td>24</td>
<td>86</td>
<td>40</td>
<td>27</td>
<td>45</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>WQ $T_1$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>29</td>
<td>0</td>
<td>18</td>
<td>27</td>
<td>0</td>
<td>9</td>
<td>17</td>
<td>16</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>AC $T_2$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>60</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>9</td>
<td>4</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>OQ $T_2$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>56</td>
<td>7</td>
<td>5</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>WQ $T_1$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>AC $T_2$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>26</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>OQ $T_2$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>WQ $T_1$ Ta</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14</td>
<td>10</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.21 Statistical data of dimples in tensile tested, irradiated 1.4914 steel [Heat treatment II]

<table>
<thead>
<tr>
<th>Samples</th>
<th>$f$</th>
<th>$\overline{d}$ (µm)</th>
<th>$\overline{x}$ (µm)</th>
<th>$N$</th>
<th>$\frac{1}{\overline{x}}$ (µm)$^{-1}$</th>
<th>$\frac{1}{\overline{x}}$ (µm)$^{-1}$</th>
<th>$d_{\text{crit}}$</th>
<th>$\sigma_F$</th>
<th>$\sigma_Y$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC $T_2$ $B$</td>
<td>.23</td>
<td>1.68</td>
<td>3.05</td>
<td>121</td>
<td>.4486</td>
<td>.31</td>
<td>1.3E-5</td>
<td>409</td>
<td>35.6</td>
<td>16.3</td>
</tr>
<tr>
<td>OQ $T_3$ $B$</td>
<td>.31</td>
<td>3.24</td>
<td>5.2</td>
<td>204</td>
<td>.12168</td>
<td>.43</td>
<td>2.2E-5</td>
<td>436</td>
<td>58.3</td>
<td>13.97</td>
</tr>
<tr>
<td>WQ $T_1$ $B$</td>
<td>.28</td>
<td>2.37</td>
<td>3.6</td>
<td>476</td>
<td>.6554</td>
<td>.55</td>
<td>1.6E-3</td>
<td>393</td>
<td>90.4</td>
<td>12.2</td>
</tr>
<tr>
<td>AC $T_2$ $B$</td>
<td>.23</td>
<td>2.1</td>
<td>4.3</td>
<td>329</td>
<td>.294</td>
<td>.48</td>
<td>2.1E-5</td>
<td>530</td>
<td>109.7</td>
<td>14.86</td>
</tr>
<tr>
<td>WQ $T_1$ $B$</td>
<td>.19</td>
<td>1.54</td>
<td>5.1</td>
<td>122</td>
<td>.5385</td>
<td>.6</td>
<td>1.8E-3</td>
<td>649</td>
<td>46.9</td>
<td>17.8</td>
</tr>
<tr>
<td>AC $T_3$ $B$</td>
<td>.23</td>
<td>2.64</td>
<td>5.3</td>
<td>235</td>
<td>.21299</td>
<td>.43</td>
<td>4.3E-5</td>
<td>681</td>
<td>103.8</td>
<td>6.2</td>
</tr>
<tr>
<td>WQ $T_2$ $B$</td>
<td>.38</td>
<td>4.4</td>
<td>1.44</td>
<td>160</td>
<td>.0679</td>
<td>.83</td>
<td>4.0E-3</td>
<td>658</td>
<td>42.8</td>
<td>14.8</td>
</tr>
<tr>
<td>OQ $T_2$ $B$</td>
<td>.19</td>
<td>3.26</td>
<td>5.45</td>
<td>109</td>
<td>.13784</td>
<td>.43</td>
<td>2.5E-3</td>
<td>429</td>
<td>75.4</td>
<td>13.4</td>
</tr>
</tbody>
</table>

- $f$ = diple vol. fraction
- $\overline{d}$ = mean diple diameter
- $\overline{x}$ = mean inter-diple spacing
- $N$ = number of dimples analyzed
- $\rho$ = diple density
- $\sigma_F$ = fracture stress
- $\sigma_Y$ = tensile yield strength
- $\epsilon$ = total elongation
- $T_B$ = tensile test at 600°C
- $T_J$ = tempering at 750°C
- $T_2$ = tempering at 700°C
- $T_3$ = tempering at 650°C
- $\eta$ = tensile test at 500°C
Table 3.22 Statistical data of dimples in unirradiated 1.4914 steel [Heat treatment II]

<table>
<thead>
<tr>
<th>Samples</th>
<th>f</th>
<th>d (µm)</th>
<th>λ (µm)</th>
<th>N</th>
<th>( \rho \times 10^{12} )</th>
<th>( \frac{1}{\lambda} (\mu m^{-1}) )</th>
<th>( \sigma_F )</th>
<th>( \sigma_Y )</th>
<th>ε</th>
<th>( d_{crit} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC. T_3 Ta</td>
<td>.55</td>
<td>2.8</td>
<td>.23</td>
<td>336</td>
<td>.1622</td>
<td>2.09</td>
<td>838</td>
<td>168</td>
<td>4</td>
<td>6.6E-2</td>
</tr>
<tr>
<td>OQ. T_3Ta</td>
<td>.266</td>
<td>4.5</td>
<td>6.3</td>
<td>359</td>
<td>.06594</td>
<td>.39</td>
<td>918.7</td>
<td>398</td>
<td>4.8</td>
<td>16.6E-3</td>
</tr>
<tr>
<td>AC. T_2Ta</td>
<td>.22</td>
<td>2.9</td>
<td>5.9</td>
<td>589</td>
<td>.15268</td>
<td>.62</td>
<td>761</td>
<td>184</td>
<td>5.7</td>
<td>11E-3</td>
</tr>
<tr>
<td>AC. T_1Ta</td>
<td>.25</td>
<td>3.45</td>
<td>7.1</td>
<td>475</td>
<td>.11007</td>
<td>.38</td>
<td>682</td>
<td>178</td>
<td>3</td>
<td>22E-3</td>
</tr>
<tr>
<td>OQ. T_1Ta</td>
<td>.374</td>
<td>2.72</td>
<td>1.15</td>
<td>398</td>
<td>.17167</td>
<td>.93</td>
<td>691.7</td>
<td>160.7</td>
<td>6.8</td>
<td>1.6E-3</td>
</tr>
<tr>
<td>WQ. T_1Ta</td>
<td>.18</td>
<td>3.44</td>
<td>4.9</td>
<td>608</td>
<td>.10738</td>
<td>.45</td>
<td>646</td>
<td>121</td>
<td>7.7</td>
<td>5.7E-3</td>
</tr>
<tr>
<td>AC. T_3TB</td>
<td>.61</td>
<td>3.1</td>
<td>2.9</td>
<td>139</td>
<td>.129098</td>
<td>.59</td>
<td>480</td>
<td>208</td>
<td>3.4</td>
<td>5.6E-3</td>
</tr>
<tr>
<td>OQ. T_3TB</td>
<td>.269</td>
<td>3.06</td>
<td>4.8</td>
<td>190</td>
<td>.13509</td>
<td>.46</td>
<td>669.5</td>
<td>91.5</td>
<td>6</td>
<td>7.6E-3</td>
</tr>
<tr>
<td>AC. T_2TB</td>
<td>.33</td>
<td>2.79</td>
<td>3.97</td>
<td>284</td>
<td>.163158</td>
<td>.5</td>
<td>548</td>
<td>162</td>
<td>4.6</td>
<td>6.5E-3</td>
</tr>
<tr>
<td>OQ. T_2TB</td>
<td>.379</td>
<td>3.79</td>
<td>2.59</td>
<td>87</td>
<td>.08862</td>
<td>.62</td>
<td>550.9</td>
<td>260</td>
<td>5.8</td>
<td>5.4E-3</td>
</tr>
<tr>
<td>OQ. T_1TB</td>
<td>.39</td>
<td>4.1</td>
<td>1.9</td>
<td>213</td>
<td>.07686</td>
<td>.73</td>
<td>504.7</td>
<td>253.7</td>
<td>7.5</td>
<td>1.0E-3</td>
</tr>
<tr>
<td>WQ. T_1TB</td>
<td>.33</td>
<td>6.4</td>
<td>4.3</td>
<td>180</td>
<td>.032789</td>
<td>.48</td>
<td>460</td>
<td>112</td>
<td>6</td>
<td>6.5E-3</td>
</tr>
</tbody>
</table>

Table 3.23 Statistical data of carbide particles in 1.4914 steel after tensile fracture [Heat treatment II]

<table>
<thead>
<tr>
<th>Samples</th>
<th>f</th>
<th>( \bar{d} ) (µm)</th>
<th>( \bar{\lambda} ) (µm)</th>
<th>( \frac{1}{\bar{\lambda}} (\mu m^{-1}) )</th>
<th>P</th>
<th>( \bar{\rho} \times 10^{12} )</th>
<th>( d_{crit} )</th>
<th>ε</th>
<th>( \sigma_F )</th>
<th>( \sigma_Y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC. T_0 Tb</td>
<td>.057</td>
<td>.16</td>
<td>4.7</td>
<td>.46</td>
<td>52</td>
<td>47.17</td>
<td>1E-3</td>
<td>4</td>
<td>849</td>
<td>228</td>
</tr>
<tr>
<td>OQ. T_0 Tb</td>
<td>.06</td>
<td>.032</td>
<td>.84</td>
<td>1.1</td>
<td>600</td>
<td>806.45</td>
<td>2E-3</td>
<td>5.9</td>
<td>821</td>
<td>222</td>
</tr>
<tr>
<td>WQ. T_0 Tb</td>
<td>.2</td>
<td>.035</td>
<td>.17</td>
<td>2.4</td>
<td>706</td>
<td>568.5</td>
<td>.3E-3</td>
<td>5.2</td>
<td>767</td>
<td>132</td>
</tr>
<tr>
<td>OQ. T_2 Tb</td>
<td>.029</td>
<td>.011</td>
<td>.34</td>
<td>1.7</td>
<td>101</td>
<td>17505</td>
<td>0.5E-3</td>
<td>6</td>
<td>670</td>
<td>91.5</td>
</tr>
<tr>
<td>OQ. T_3 Tb</td>
<td>.0087</td>
<td>.013</td>
<td>1.39</td>
<td>.85</td>
<td>54</td>
<td>8709.82</td>
<td>4E-3</td>
<td>4.8</td>
<td>919</td>
<td>399</td>
</tr>
<tr>
<td>WQ. T_3 Tb</td>
<td>.076</td>
<td>.033</td>
<td>.37</td>
<td>1.64</td>
<td>295</td>
<td>1177.8</td>
<td>0.6E-3</td>
<td>5.3</td>
<td>606</td>
<td>114</td>
</tr>
</tbody>
</table>

\( \bar{d} \) = untempered

\( T_3 = 650^\circ C \) tempering

P = number of particles analysed

\( \bar{\rho} \) = particle density

ε = total strain at fracture

\( d_{crit} \) = critical carbide diameter
Table 3.24 Vickers hardness test data for aged and non-aged 1.4914 steel [Heat treatment II]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling rate °C/sec</th>
<th>Tempering temperature</th>
<th>$H_v$</th>
<th>$H_n$</th>
<th>$\Delta h$</th>
<th>$\delta$</th>
<th>$\varepsilon_{unirr}$ (%)</th>
<th>$\varepsilon_{irr}$ (%)</th>
<th>$\Delta C$ (°C)</th>
<th>$\sigma_{y_{unirr}}$ (MPa)</th>
<th>$\sigma_{y_{irr}}$ (MPa)</th>
<th>$\Delta f_{y}$</th>
<th>$\eta$</th>
<th>$\alpha$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A AC</td>
<td>T3</td>
<td>226.71</td>
<td>335.2</td>
<td>-109</td>
<td>4</td>
<td>9.2</td>
<td>+5.2</td>
<td>168.2</td>
<td>50.2</td>
<td>118</td>
<td>1.3</td>
<td>.33</td>
<td>25.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2A OQ</td>
<td>T3</td>
<td>217.21</td>
<td>350.7</td>
<td>-133</td>
<td>4.8</td>
<td>8.5</td>
<td>+3.7</td>
<td>398</td>
<td>24.7</td>
<td>373.3</td>
<td>.77</td>
<td>.38</td>
<td>49.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3A WQ</td>
<td>T3</td>
<td>179.53</td>
<td>339</td>
<td>-160</td>
<td>2</td>
<td>9.6</td>
<td>+7.6</td>
<td>261.5</td>
<td>12.6</td>
<td>248.9</td>
<td>3.8</td>
<td>.47</td>
<td>12.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 AC</td>
<td>T3</td>
<td>203</td>
<td>309</td>
<td>-106</td>
<td>4</td>
<td>9.2</td>
<td>+5.2</td>
<td>168.2</td>
<td>50.2</td>
<td>118</td>
<td>1.3</td>
<td>.34</td>
<td>26.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 AC</td>
<td>T2</td>
<td>177.72</td>
<td>328.2</td>
<td>-151</td>
<td>5.7</td>
<td>7.45</td>
<td>+1.75</td>
<td>184.2</td>
<td>26.8</td>
<td>157.4</td>
<td>.31</td>
<td>.46</td>
<td>.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 AC</td>
<td>T1</td>
<td>213.53</td>
<td>357</td>
<td>-104</td>
<td>3</td>
<td>8.80</td>
<td>+5.88</td>
<td>178</td>
<td>69.2</td>
<td>108.8</td>
<td>1.96</td>
<td>.4</td>
<td>20.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 OQ</td>
<td>T3</td>
<td>199.72</td>
<td>337.9</td>
<td>-138</td>
<td>4.8</td>
<td>8.5</td>
<td>+3.7</td>
<td>398</td>
<td>24.7</td>
<td>373.3</td>
<td>.77</td>
<td>.41</td>
<td>53.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 OQ</td>
<td>T2</td>
<td>209.52</td>
<td>309.3</td>
<td>-100</td>
<td>4</td>
<td>7.5</td>
<td>+3.5</td>
<td>189</td>
<td>41.5</td>
<td>147.5</td>
<td>.88</td>
<td>.32</td>
<td>36.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 OQ</td>
<td>T1</td>
<td>207.55</td>
<td>319.2</td>
<td>-112</td>
<td>6.8</td>
<td>8.8</td>
<td>+2</td>
<td>168.7</td>
<td>42.8</td>
<td>125.9</td>
<td>.29</td>
<td>.35</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 WQ</td>
<td>T3</td>
<td>191.75</td>
<td>322</td>
<td>-131</td>
<td>2</td>
<td>9.6</td>
<td>+7.6</td>
<td>261.5</td>
<td>12.6</td>
<td>248.9</td>
<td>3.8</td>
<td>.41</td>
<td>10.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 WQ</td>
<td>T2</td>
<td>206.55</td>
<td>314.2</td>
<td>-108</td>
<td>3.9</td>
<td>9.1</td>
<td>+5.2</td>
<td>239.5</td>
<td>33.3</td>
<td>206.2</td>
<td>1.33</td>
<td>.36</td>
<td>.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 WQ</td>
<td>T1</td>
<td>208.52</td>
<td>314.2</td>
<td>-106</td>
<td>7.7</td>
<td>7.3</td>
<td>-0.4</td>
<td>121.8</td>
<td>71.8</td>
<td>49.2</td>
<td>-.05</td>
<td>.34</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 = irradiation hardening opposing thermal effect
A = tensile specimens
+ = off cuts
* = 10Kg load on samples aged at 650°C for 525 hours
** = 10Kg load on samples not aged
$\varepsilon_{unirr}$ = total elongation of unirradiated samples
$\varepsilon_{irr}$ = total elongation of irradiated samples
$\sigma_{y_{unirr}}$ = tensile yield strength of unirradiated samples
$\sigma_{y_{irr}}$ = tensile yield strength of irradiated samples
$\eta$ = factor for thermal plus radiation effect on total elongation
$\alpha$ = factor for thermal effect on total elongation
$\mu$ = contribution from thermal effect on total elongation

For example:
- $c_{unirr} = \frac{\Delta h + \delta}{\varepsilon_{unirr}}$
- $c_{irr} = \frac{\Delta h + \delta}{\varepsilon_{irr}}$
- $\sigma_{y_{unirr}} = \frac{\sigma_{y_{unirr}}}{\Delta h + \delta}$
- $\sigma_{y_{irr}} = \frac{\sigma_{y_{irr}}}{\Delta h + \delta}$
- $\eta = \frac{\Delta h + \delta}{\varepsilon_{unirr}}$
- $\alpha = \frac{\Delta h + \delta}{\varepsilon_{irr}}$
- $\mu = \frac{\Delta h + \delta}{\varepsilon_{unirr}}$
- $\eta = \frac{\Delta h + \delta}{\varepsilon_{irr}}$
- $\alpha = \frac{\Delta h + \delta}{\varepsilon_{unirr}}$
- $\mu = \frac{\Delta h + \delta}{\varepsilon_{irr}}$
Table 3.4 Fracture toughness data for uncracked 14914 steel [Heat treatment II]

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Cracking rate °C/sec</th>
<th>Cooling rate °C/sec</th>
<th>Tempering temp. °C</th>
<th>Tensile test temp, °C</th>
<th>( \gamma ) (%)</th>
<th>( \delta ) (( \mu )m)</th>
<th>( \sigma_{y} ) (M Pa)</th>
<th>( \sigma_{f} ) (M Pa)</th>
<th>( \gamma_{c} ) (M Pa)</th>
<th>( \tau_{0} ) (M Pa)</th>
<th>( \epsilon_{y} ) (M Pa)</th>
<th>( \epsilon_{f} ) (M Pa)</th>
<th>( k_{c} ) (M Pa m^{1/2})</th>
<th>( J_{c} ) (M Pa m^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Gmean = \( \frac{G_{ferritic}}{G_{0.65}} \)

\( \sigma_{y} \) = tensile yield strength
\( \sigma_{f} \) = stress at interface before decohesion
\( \epsilon_{y} \) = average shear strain
\( \epsilon_{f} \) = effective strain at interface before decohesion
\( \gamma \) = dimensional proportionality factor (\( \gamma \) = working fracture toughness)
\( \gamma_{c} \) = critical crack opening displacement
\( \delta \) = crack opening displacement

\( \epsilon = \frac{1}{(1+v)(1-2v)} \)

\( \epsilon \) = Poisson ratio

\( \nu = 0.3 \) = Poisson ratio

\( \nu = 0.3 \) = Poisson ratio

\( \nu = 0.3 \) = Poisson ratio

\( \nu = 0.3 \) = Poisson ratio

\( \nu = 0.3 \) = Poisson ratio

\( \nu = 0.3 \) = Poisson ratio
<table>
<thead>
<tr>
<th>Sample label</th>
<th>Sample number</th>
<th>Cooling temp. °C/sec</th>
<th>Tempering temp. °C</th>
<th>Tensile test temp. °C</th>
<th>(μm)</th>
<th>(μm)</th>
<th>(μm²)</th>
<th>(μm²)</th>
<th>(μm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC 1</td>
<td>47</td>
<td>T, a</td>
<td></td>
<td></td>
<td>4.6</td>
<td>322</td>
<td>1.18</td>
<td>.033</td>
<td>1.39</td>
</tr>
<tr>
<td>DQ 2</td>
<td>115</td>
<td>T, a</td>
<td></td>
<td></td>
<td>4.2</td>
<td>134</td>
<td>.81</td>
<td>.058</td>
<td>.66</td>
</tr>
<tr>
<td>WQ 3</td>
<td>346</td>
<td>T, a</td>
<td></td>
<td></td>
<td>6.8</td>
<td>310</td>
<td>1.13</td>
<td>.027</td>
<td>1.27</td>
</tr>
<tr>
<td>AC 4</td>
<td>47</td>
<td>T, a</td>
<td></td>
<td></td>
<td>3.7</td>
<td>160</td>
<td>.94</td>
<td>.053</td>
<td>.88</td>
</tr>
<tr>
<td>DQ 5</td>
<td>115</td>
<td>T, a</td>
<td></td>
<td></td>
<td>3.75</td>
<td>803</td>
<td>2.08</td>
<td>.003</td>
<td>4.3</td>
</tr>
<tr>
<td>WD 6</td>
<td>346</td>
<td>T, a</td>
<td></td>
<td></td>
<td>4.55</td>
<td>164</td>
<td>.84</td>
<td>.049</td>
<td>.71</td>
</tr>
<tr>
<td>AC 7</td>
<td>47</td>
<td>T, a</td>
<td></td>
<td></td>
<td>4.44</td>
<td>560</td>
<td>1.59</td>
<td>.007</td>
<td>2.7</td>
</tr>
<tr>
<td>DQ 8</td>
<td>115</td>
<td>T, a</td>
<td></td>
<td></td>
<td>4.4</td>
<td>160</td>
<td>.85</td>
<td>.049</td>
<td>.72</td>
</tr>
<tr>
<td>DQ 11</td>
<td>115</td>
<td>T, B</td>
<td></td>
<td></td>
<td>6.9</td>
<td>1240</td>
<td>1.94</td>
<td>.0028</td>
<td>3.76</td>
</tr>
<tr>
<td>WQ 12</td>
<td>346</td>
<td>T, B</td>
<td></td>
<td></td>
<td>6.1</td>
<td>130</td>
<td>.68</td>
<td>.068</td>
<td>.46</td>
</tr>
<tr>
<td>AC 13</td>
<td>47</td>
<td>T, B</td>
<td></td>
<td></td>
<td>4.1</td>
<td>660</td>
<td>1.8</td>
<td>.0067</td>
<td>3.24</td>
</tr>
<tr>
<td>DQ 14</td>
<td>115</td>
<td>T, B</td>
<td></td>
<td></td>
<td>6.7</td>
<td>1600</td>
<td>2.22</td>
<td>.0018</td>
<td>4.9</td>
</tr>
<tr>
<td>WQ 15</td>
<td>346</td>
<td>T, B</td>
<td></td>
<td></td>
<td>7.4</td>
<td>160</td>
<td>.66</td>
<td>.07</td>
<td>.44</td>
</tr>
<tr>
<td>AC 16</td>
<td>47</td>
<td>T, B</td>
<td></td>
<td></td>
<td>7.43</td>
<td>1750</td>
<td>2.17</td>
<td>.001</td>
<td>0.7</td>
</tr>
<tr>
<td>DQ 17</td>
<td>115</td>
<td>T, B</td>
<td></td>
<td></td>
<td>6.95</td>
<td>220</td>
<td>.79</td>
<td>.055</td>
<td>.62</td>
</tr>
<tr>
<td>WD 18</td>
<td>346</td>
<td>T, B</td>
<td></td>
<td></td>
<td>8.09</td>
<td>1970</td>
<td>1.55</td>
<td>.006</td>
<td>2.4</td>
</tr>
<tr>
<td>WQ 20</td>
<td>115</td>
<td>T, γ</td>
<td></td>
<td></td>
<td>7.9</td>
<td>289</td>
<td>.86</td>
<td>.002</td>
<td>.74</td>
</tr>
<tr>
<td>AC 21</td>
<td>346</td>
<td>T, γ</td>
<td></td>
<td></td>
<td>8.24</td>
<td>18</td>
<td>.66</td>
<td>.046</td>
<td>.44</td>
</tr>
<tr>
<td>DQ 22</td>
<td>47</td>
<td>T, γ</td>
<td></td>
<td></td>
<td>8.03</td>
<td>610</td>
<td>1.2</td>
<td>.024</td>
<td>2.44</td>
</tr>
<tr>
<td>WD 24</td>
<td>346</td>
<td>T, γ</td>
<td></td>
<td></td>
<td>8.24</td>
<td>198</td>
<td>.69</td>
<td>.06</td>
<td>.476</td>
</tr>
<tr>
<td>AC 25</td>
<td>47</td>
<td>T, γ</td>
<td></td>
<td></td>
<td>5.6</td>
<td>300</td>
<td>1.04</td>
<td>.012</td>
<td>1.08</td>
</tr>
<tr>
<td>WQ 27</td>
<td>346</td>
<td>T, γ</td>
<td></td>
<td></td>
<td>7.7</td>
<td>860</td>
<td>1.47</td>
<td>.009</td>
<td>2.22</td>
</tr>
</tbody>
</table>
Appendix I

RNOD (1.4914)

Chg. 10045

Austenitisierung: 1080°C - 20 min Abschreckkorngröße: 6 - 7

<table>
<thead>
<tr>
<th>Ac₁₈ (9.4°C/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1080°C - 20 min</td>
</tr>
</tbody>
</table>

Intensität der Karbidausscheidung

Ac₀₉ (0.4°C/min.)

λ = 0.07

10 mm dimensions

Austenitisierung: 1075°C - 20 min Abschreckkorngröße: 9 - 10, vereinzelt 7 - 9

<table>
<thead>
<tr>
<th>Ac₁₈ (0.4°C/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1075°C - 20 min</td>
</tr>
</tbody>
</table>

Intensität der Karbidausscheidung

Ac₀₉ (0.4°C/min.)

λ = 0.01

Öl 0.06

Luft 1.0

Abkühlung von ≤ 10mm

A-K = Bereich des Austenits u. Karbids

F+K = Bereich der Ferrit u. Karbimbildung

M = Bereich der Perlitbildung

Kgm = Komgrenzenmartensit

P = Bereich der Martensitbildung

0.03 - 7.6 = Abläufungsparameter λ

Fig. A.0.0 Kontinuierliche ZTU - Schaubilder

After M. Schirra (1984)
Fig. A.0.1 Two basic phase diagrams

(a) $\Delta H$ negative, $H_{\alpha Y} > Y -$ favoured
(b) $\Delta H$ positive, $H_{\alpha Y} < Y -$ favoured

After Zener, In Andrews JISI (1956) 184, 414

---

Fig. A.0.2 Effect of manganese and molybdenum on the kinetics of the ferrite reaction [Kinsman and Aaronson (1967)].
Fig. A.0.3 Carbide constitution in 0.2% C steels at 700 C as a function of vanadium and chromium content (Shaw and Quarrell, JISI, 1957, 185, 10).

Fig. A.0.4 The effect of carbon on $M_s$ and $M_f$ (Petty ed) Martensite : Fundamentals and Technology, Longmans 1970).
Fig. A.0.5 Effect of carbon content on the type of martensite and the amount of retained austenite in Fe-C alloys (Speich, Met. Trans. 1972) 3, 1045.

Fig. A.0.6 Free-energy of austenite and martensite as a function of temperature. Kaufmann and Cohen, Progress in Metal Physics (1958), 2, 165.
Fig. A.0.7 Effect of tempering for 1 h on the mechanical properties of a 12Cr-1Ni-0.2C stainless steel. Typical results for 50 mm diameter bars, oil-quenched (Thelning, Steel and its Heat Treatment, Bofors Handbook, Butterworths, 1975)
Fig. A.0.8  TTT diagram of a molybdenum steel 0.4C, 0.2Mo
Butterworths, 1975)
Fig. A.0.9  TTT diagram of a molybdenum steel. 0.3C, 2.0Mo
(Thermal Steel and its Heat Treatment, Bofors Handbook, Butterworths 1975.)
Fig. A.10. Free energy change for the austenite-martensite reaction as a function of temperature and carbon content (Kaufmann and Cohen, *Progress in Metal Physics*, 1958, 7:165)
Fig.A.0.11 Effect of alloying elements in the bainite reaction TTT curves: a. schematic diagram of a low carbon steel (Irvine and Pickering, JIS, 1957, 187, 292)
FIGURE A.1.3a  Schematic diagram showing the operating principle of the field emission gun used on the Phillips EM400(STEM)
FIGURE A.1.3b: Stationary diffraction pattern formation in STEM.
FIGURE A.1.3: The electron Optical System and Signal Detectors in an AEM
FIGURE A.1.5 Illustration of thresholding

A. Over Detected  D. Scanner Video
B. Under Detected  E. Squared Video
C. Correctly Detected

FIGURE A.1.6 Autodelineation
APPENDIX 3

The computer programme in A2.1 and A2.2 is designed to produce quantitative measurement of solute segregation via a combined equilibrium and non-equilibrium mechanism. A2.1, when operated will produce an isometric plots showing dependence of solute segregation on two main parameters (i) solution treatment temperature and (ii) cooling rates whereas A2.2 will produce two dimensional plots indicating solute segregation as a function of ageing time.

The programme is based on the following equations

\[ C_b = C_g \exp \frac{E_b}{kT} \left( 1 + C_g \exp \frac{E_b}{kT} \right)^{-1} \]  

A3.1

where \( E_b \) = binding energy of impurity to the lattice

\( C_b \) = concentration of impurity in a monolayer on interfaces

\( T \) = temperature

\( C_g \) = concentration of impurity in the matrix alloy

\( k \) = Boltzmann's constant

From McLean

\[ \frac{C_x - C_g}{C_b - C_g} = 1 - \exp \left[ -\frac{4D_I t}{\alpha^2 d_i} \right] \operatorname{erfc} \left[ \frac{4D_I t}{\alpha^2 d_i} \right] \]  

A3.2

where \( C_x \) = concentration of impurity on the boundary after time \( t \),

\[ \alpha = \frac{C_b}{C_g} \]  

A3.3

\( d_i \) = width of the boundary (2.5 x 10^{-10} m)

\( D_I \) = diffusivity of the impurity in the matrix

\( t \) = time

Segregation by equilibrium process is obtained by summation of \( E_s \) in quench and \( E_s \) during ageing.
To obtain segregation amount in quench, the expression

$$T = T_i \exp \left( \frac{-t}{\tau} \right)$$

was used, where \( \tau = \frac{1000}{\Theta} \)

\( t = \text{time}, \ T_i = \text{solution treatment temperature} \)

cooling rate range is assumed as \( 0 - 100 \text{ s}^{-1} \)

\( T = T_i \times 0.26 \) is also assumed

ES = Equilibrium Segregation

Equation A3.1 was used to obtain ES during ageing.

Combined ES in quench and age can be obtained as

$$C_x(ES) = C_xQ + C_x\text{age}$$

Non-equilibrium Segregation (NES)

$$\frac{C_x - C_g}{C_b - C_g} = \frac{\text{erfc}[\frac{x}{2(D_v t)^{1/2}}]}{2(D_v t)^{1/2}}$$

$$C_b = \exp \left( \frac{E_b - E_F}{kT_i} - \frac{E_b - E_F}{kT} \right) \cdot \frac{E_b}{E_F}$$

where \( E_b = \text{Difference between the sum of vacancy and impurity formation energies and the formation energy of the vacancy - impurity complex} \)

\( E_F = \text{energy of formation of a vacancy in the matrix} \)

\( T_{0.5TM} = \text{the temperature at which sufficient diffusion to allow NES to occur becomes insignificant} \)

\( D_v = \text{diffusion coeff. for vacancy - impurity complexes in the matrix} \)

$$t = \frac{RkT_i^2}{\Theta E_A}$$

\( t = \text{effective time}; \ \Theta = \text{quench rate} \)

\( E_A = \text{average of the activation energies for diffusion of impurities and vacancies in the matrix}. \ R = \text{constant} = 0.01 \)
Allowing for ageing after cooling
then

\[ t_A = T_A \exp \left[ -\frac{E_A (T_i - T_A)}{k T_i T_A} \right] \]  \hspace{1cm} A3.9

A critical time \( t_c \), above which desegregation occurs is

\[ t_c = \frac{\delta^2 \ln \left( \frac{D_v}{D_I} \right)}{4(D_v-D_I)} \]  \hspace{1cm} A3.10

where \( \delta \) is a constant (equal to \( 5 \times 10^{-2} \))

\[ d = \text{grain size} \]

Hence,

The desegregation equation for \( t > t_c \) is

\[ \frac{C_x - C_g}{C_b - C_g} = \left[ \frac{D_v t_c}{D_I t} \right]^\frac{1}{2} \exp \left[ -\frac{x^2}{4D_I t} \right] \]  \hspace{1cm} A3.11

Total segregation amount, \( F \), can be obtained as

\[ F = \frac{C_x(ES)}{4} + C_x(NES) \]  \hspace{1cm} A3.12

\[ D = \Delta S \exp \left[ -\Delta Q \right] \]

\[ \Delta S = \frac{1}{12} A.d \]

\[ \Delta S = \text{entropy term} \]

\[ A.d = \text{entropy term for self diffusion in matrix} \]

\[ \frac{1}{12} \] - from co-ordination number relating to the number of bonds per defect.
For details about these calculations see Faulkner (1987a).

The list of constants in the programme are therefore:

- $r = \text{constant} = R$
- $e_a = \text{Average activation energies - impurities and vacancies (} E_A \text{)}$
- $a = \Delta S$ entropy term for diffusion
- $q = \Delta Q$ average activation energy for diffusion
- $a_i = \Delta S$ Impurities
- $q_i = \Delta Q$
- $t_i = \text{Solution treatment temperature}$
- $t_{\text{step}} = \text{Temperature step}$
- $\text{Cool}_i = \text{Cooling rate}$
- $C_{\text{step}} = \text{Cooling rate step}$
- $e_b = \text{binding energy, matrix - impurity}$
- $e_r = \text{formation energy for vacancy}$
- $C_g = \text{Impurity concentration (fractional term)}$
- $\delta = \text{constant}$
- $g = \text{grain size}$
- $t_a = \text{Ageing temperature}$
- $t_{\text{imag}} = \text{Ageing time}$
library 'ainosurt'
c library 'aino'
c library 'vafpol'
c library 'lusunv'
c
program to calculate separation

non equilibrium and equilibrium combined

dimension t(50), cool(50), t(50), x(1030), f(50,70), ittitle(6),
1(10000),
t(70), cxe(70), almha(70), da(70), tim(50), h(50,70), tm(170),
3erf(50,70), x(50,70), n(50,70), o(70), cxe(50,70), fe(50,70),
4ql(1,50,70), t(70)

common erf, ititle
open(unit=3, file='ray5', form='formatted')
read(5,*) r
read(5,*) e
read(5,*) ap
read(5,*) qo
read(5,*) ai
read(5,*) qi
read(5,*) ti,
read(5,*) tstep
read(5,*) cooli
read(5,*) cstep
read(5,*) eb
read(5,*) ef
read(5,*) cg
read(5,*) delta
read(5,*) gs
read(5,*) ta
read(5,*) timan
read(5,*) ittitle
27 format(Aa4)
write(1,23) ititle
28 format(/,5x,634)
timah=timah/3600.
oo=oo*23069.
qi=qi*23069.
write(1,10) re, ap, ro, ai, qs, ef, cg, delta, ta, timan
10 format(2x,2n16.4/e2x,3heal=e6.4/r2x,2heav/e2x,3hao=e10.4,2x,16hn=,e2x,3hao=e6.0/r2x,7hel/mol/e2x,3hao=e10.4,2x,2n=+r2x,2x,thmi=

1/sr,fo,2x,7hel/mol/e2x,3hao=e6.4/r2x,2heav/e2x,2x,2x,3haf=/
4.6,4/r2x,2heav/e2x,2x,2x,3helmol/e2x,3n=+a5.1/r2x,7microns,
6/2x,9haq time=6.0/r2x,1hke,2x,9haq time=5.0/r2x,5hke

call c11n1

c
t(a)=
f(x,)=

c=a*1.e=e

timah=timah/3600.
c
es in ape

e1=eb/(r,6e-5*ta)
cxe1=(e1*exp(a1))/(1.,+c2,exp(a1))
dal=a1*exp(-al,c1,2,ta))
cxun1=cxe1/cq

c2=(4.,9al*timah)/(c1a31e1*2.,(do+2.,))a+.5

call erf(x,1)
erf1=1.-erf1
c12=.01+2.
if(a12>0.30) go to 91
ex1=exp((a1+a1*timaw)/(alnol+a1*(cot+2.)))
go to 90
91 ex1=1.0+20.
68 h1=ex1*erf*k
p1=ex11-c
ex2=(c1*h1)

nes in age and quench

do 7 k=1,76
tn(k)=ti+tstep*(k-1)
tproj=ti+60*tstep
write(193) tnn(k)
73 format(/'10x,'temperature',2x,f6.1,'2x,'degrees kelvin')
cool(i)=0
do 6 i=1,50
fi(k)=0.0
fe(i,k)=0.0
cool(i)=cool+ctsto*(i-1)
corho=cool+4*ctsto
write(1,8) cool(i)
6 format(1X,'cooling rate',2x,f12.7,2x,'degrees/second')
x(j)=1.e-9
do 5 j=1,1000
s=0.0
t=tinan*exp((-ex*(t7(k)-ta))/((8.65-5)*ta(ta(k)*ta))
if(j-1)13,14,15
13 x(j)=1.e-9
go to 15
14 x(j)=(j)*1.e-8
15 t(i)=(r*8.65-5*(t7(k)+2)/cool(i)*ex)+s
ar=ap*exp(-1/cool(i)*ex))
di=ai*exp(-(n)/?*tn(k)))
a=exp(-(1/j)*2)/(4.*dist*(j))
b=x(j)/(2.*sort*(d2*ti(i)))
call erfx(b)
erf=1.-erf
tc=delta*(n*2)*aln(cm/i)/(4.*(cm-di))
tn=cm-eff)/(8.655*tan(k))
v=cm-eff)/(8.652)
q1=(pl*exp(u-v))/ef
ch=pl*cn
c=ch-cq
c=sort*(d2*tc/(3.141593*di*t(i)))
if(t(i).lt.tc) go to 2
if(t(i).gt.tc) go to 1
1 cx1=c*d*a
9o to 3
2 cx1=c*erf
3 cx=cx1+c
if(i-1)1,1,12
12 if(cx1<at.01e) go to 18
11 x(j)=x(j)+1.e10
write(1,4) x(i),cx
4 format(2x,2x='2*x**2,1.2x9hanstroms,2**3ncx=x1,1.4)
if(j-1)13,1,14
18 if(j-10)17,17,1y
17 (i,cx)=cx1+1(i,c)
go to 5
19 f(i,k)=f(i,k)
5 continue
  c write(1,96) t(i,k)
25 format(3,4)
  c es in sequen
97 t11(k)=tm(k)-773.
t12(k)=(tm1(k)+2A)+273.
e(k)=kb/((9.06-5*t12(k))
cx1(k)=(cx+exa(e(k)))/((1.+ca*exa(e(k)))
alpha(k)=cx1(k)/c7
wo=2.5e-17
di(k)=ai*exa(ai/(2.+tm2(k)))
ti1(i)=t70.*cool(i)
ti2(k)=(4.+x2(k)*ti1(i))/((alpha(k)*2.)*(c0+2.))**.5
  call erfx(a(i,k))
erfe(i,k)=1.-erfuc
11(i,k)=c(i,k)*2.5
if(i1(i,k)=1.710) go to 9
ex(i,k)=exa((4.+d2a(k)*ti1(i))/((alpha(k)*2.)*(c0+2.)))
go to 50
9 ex(i,k)=1.0*x20.
50 hi(i,k)=1.-(-ex(i,k)*erfe(i,k))
u(k)=cx1(k)-c0
cx(i,k)=n(k)*u(i,k)
fe(i,k)=(cx2+cx(i,k))/4.
  call write(1,95) fe(i,k)
95 format(3,4)
t(i,k)=15.*f(i,k)+fe(i,k)
6 continue
7 continue
  mnin=f(1,1)
fmix=f(1,1)
do 25 k=1,71
do 25 i=1,50
  if(f(i,k)-fmax)<5.333577
25 if(mnin-f(i,k))>253296
  fmix=f(i,k)
max=f(i,k)
go to 29
29 fmint=f(i,k)
go to 29
27 fmax=f(i,k)
go to 29
29 continue
  go 25 k=1,71
  go 25 i=1,50
  if(ti2a(i,k)=1.7,2,2)
 22 write(1,15)i=x(cool(i),f(i,k),2a(i,k)
15 format(4,8.1x2,cooling rate=,f9.4,2x,int=,f10.6,21'int=,1,10,n)
go to 20
20 write(1,24)i=x(cool(i),f(i,k),2a(i,k)
24 format(4,8.1x2,cooling rate=,f11.4,2x,int=,f10.6,21'int=,1,10,n)
21 continue
call nicle
  call errmax(51)
call titlo(4,6,111)
call subsc(i,111,1)
CALL ISNORJ(50, COOLISCPROI, TIT, TURNF, M, N, I, J, W)
CALL TIT
CALL DEVARC
READ(1, 30) N
30 FORMAT(I1)
STOP
END

SUBROUTINE ERFX(X)
COMMON ERF, TITLE(11)
IF(X.GT.6.) GO TO 21
IF(X.LT.-6.) GO TO 22
IF(X.GT.1.5) GO TO 4
IF(X.LT.-1.5) GO TO 4
Y=X+((X**5.)/10.)+((X**9.)/215.)+((X**13.)/9350.)
Z=((X**3.)/3.)+((X**7.)/42.)+((X**11.)/132.)+((X**15.)/756.)
ERFC=(Y-Z)*Z/SORT(3.14159)
GO TO 3
4 ERFC=1./(SORT(3.14159)*X*EXP(X**2.))
GO TO 3
21 ERFC=1.
GO TO 3
22 ERFC=-1.
3 RETURN
END

SUBROUTINE TIT
COMMON ERF, TITLE(6)
CALL NAPENO(X,Y,VI)
CALL CHAENC(TITLE, YNSAIT, ENQ)
Y=YO-2.*H
X=0.5*(X+X+X)*W
CALL MOVEC(X,Y)
CALL CHAARR(TITLE, 5, 4)
RETURN
END
SEGAGE: FORTRAN PROGRAM (A2.2)

C program to show the effect of ageing on segregation
C with additional equilibrium segregation screens over 1000 a
dimension t(170),x(100),x(1000),f(170),f(170)
dimension timer(100) erfc(170),x(1000),n(170),x(2(100))
f,
common erfc, title(6)
open (unit=5, file='ray5', form='formatted')
read(5,*), r
read(5,*), ea
read(5,*), ao
read(5,*), a0
read(5,*), ai
read(5,*), ci
read(5,*), ti
read(5,*), co
read(5,*), ef
read(5,*), c0
read(5,*), delta
read(5,*), ao
read(5,*), as
read(5,*), as
read(5,*), ao
read(5,*), ti
read(5,*), tao
read(5,*), tao
read(5,*), tao
read(5,*), tao
read(5,*), tao
read(5,*), tao
read(5,*), tao
read(5,*), tao
27 format (64)
write(6,1)
write(1,1)
28 format (/5x,64)
qo=no*230.69.
ci=ci*230.69.
write(1,10) r,ea,ea,ao,ai,ei,c0,delta,qo,ta
10 format (2x,2x,nr=-f6.4,2x,3he=-f6.4,2x,2he=-f6.3,3he=-e10.4,x 16he=-2.5/x,2x,3he=-f6.0,2x,7he=-e10.4,3x 2.6he=-2.5/x,2x,3he=-f6.0,2x,7he=-e10.4 2x,he=-2.5/x,2x,3he=-f6.0,2x,7he=-e10.4,3x 5/x,2x,3he=-f6.1,2x,7he=-microns.
6/2x,9hane t=n, t=th.0, t=1, th=1, th=1
qo=qo*1.0-c
do 7 x=1,100
7 tm(k)=timer+timer(k-1)
timer(k)=tm(k)/3f07.
f(k)=0
do 5 j=1,10
5 s=tv(k)+exp((-ex*(ti-ta))/((x.j-5)*ti*t))
if(i-1)13,13,14
13 x(j)=1.0-e-9
un to 15
14 x(j)=(j-1)*1.0-e-9
15 t(k)=(t(k)-6.8*5*(ti-ta))/((coolike),)+s
do=exp(-zn)/(7.2+ti)
dim=exp(-oz)/(7.2+ti)
s=exp(-(x(j)+2.0)/4.*dot(k))
px(j)=(2.*do+rt(t[k]))
6 format (/16.1,16.0,e10.4,e10.4)
call erfc(h)
erf=1-erfc
t=c*tan*(as*2)+tan(atan/ti)/((4.*30-ni))
v=(a*e-f)/((8.*ei-ti))
p=la*e-f/(8.*ni)
a1=(exp(70-6.0))
c = 0.1 * c
ch = ch
j = sort Española tierra asterisco t/3.1415 * 
if(t(k) < l) go to 2
if(t(k) = l) go to 1
1 cx1 = c * a * a
  go to 3
2 cx1 = c * erf
3 cx = cx1 + cn
if (cx < qr * 0.1 * c) go to 18
if (j = 1) 18, 18, 5
18 if (j = 10) 17, 17, 1
17 f(k) = cx1 + f(k)
  go to 5
19 f(k) = f(k)
5 continue
es in quench
tm1 = ti - 273
tm2 = (tm1 * 2.6) + 273
e = e * b / (8.6e - 5 * tm2)
cx1 = (c * cx + e) * (1 + c * cx + e)
alpha = cx1 / cg
s = 2.5e - 10
d = a * cx / (ti * 2.6)
tm1 = 200 / cooli
ar = (4 * d * a * tm1) / ((alpha * 2.4) * (d * 2.4)) * e
5 call erf
erfe = 1 - erfc
if (q * 2.4) at 30, go to 9
ex = exp(4 * d * a * tm1) / ((alpha * 2.4) * (d * 2.4))
go to 16
9 ex = 1.0 * 20
16 h = 1.0 - cx * erfe
p = cx1 - cg
cx = (p * h)
es durante acenq
el = e * b / (8.6e - 5 * ta)
cx1 = (c * cx + e) * (1 + c * cx + e)
alpha = cx1 / cg
q2 = (4 * d * a * tm(k)) / ((alpha * 2.4) * (d * 2.4)) * e
5 call erf
erfe1(k) = 1 - erfc
if (a * 2.4) at 30, go to 91
ex1(k) = exp(4 * d * a * tm(k)) / ((alpha * 2.4) * (d * 2.4))
go to 68
91 ex1(k) = 1.0 * 20
68 h1(k) = 1.0 - cx1(k) * erfe1(k)
p1 = cx1 - cg
cx2(k) = (p1 * h1(k))
fe(k) = (cx2(k) + cx) / 4
if (k = 1) 99, 99, 99
99 if (re(k) = fe(k - 1)) 92, 94, 98
92 re(k) = fe(k - 1)
98 f(k) = f(k) * f(k)
f(k) = f(k) - f(k)
7 continue
23 write(1, 26) ti, coolista
24 format(1, 16.2, 2 * g, coolista rate = 'f11.4, 2 * g, 
2 * l g, 16.0, 2 * t')
\textbf{fmin}=f(1) \\
\textbf{fmax}=f(1) \\
do 20 \textbf{k}=1,100 \\
write(1,25)\ \textbf{time}(\textbf{k}), f(\textbf{k}), f1(\textbf{k}), f2(\textbf{k}) \\
25 \textbf{format}(4x,\textbf{a}5,4x,\textbf{e}12.5,3x,\textbf{e}12.5,3x,\textbf{e}12.5,3x,\textbf{a}10,6x,2) \\
\textbf{fnes}='af1.0.,x,' \textbf{es}='af9.6) \\
if(f(\textbf{k})>\textbf{fmax}) 95,93,97 \\
if(f(\textbf{fmin})>\textbf{fmax}) 95,93,97 \\
95 \textbf{fmin}=f(\textbf{k}) \\
\textbf{fmax}=f(\textbf{k}) \\
goto 20 \\
96 \textbf{fmin}=f(\textbf{k}) \\
goto 20 \\
97 \textbf{fmax}=f(\textbf{k}) \\
20 \textbf{continue} \\
\textbf{c} do 31 \textbf{k}=1,100 \\
\textbf{c} write(1,25)\ \textbf{time}(\textbf{k}), f(\textbf{k}) \\
\textbf{c} 31 \textbf{continue} \\
\textbf{call} c1051n \\
\textbf{call} nice1 \\
\textbf{call} axiploto(\textbf{h},\textbf{m},\textbf{n},\textbf{t},\textbf{time}(1),\textbf{time}(10)), fmin, fmax \\
\textbf{11f} \textbf{aging \ time} \textbf{11h}segregation \ \textbf{intensity} \textbf{?1} \\
\textbf{call} orapol(\textbf{time}(1),f(10)) \\
\textbf{call} tit \\
\textbf{call} deveno \\
\textbf{stop} \\
\textbf{end} \\

\textbf{subroutine} \textbf{erfc}(\textbf{x}) \\
\textbf{common} \textbf{erfc},tit(\textbf{*}(11)) \\
\textbf{if} (x<ge.9.) \textbf{go} \textbf{to} \textbf{21} \\
\textbf{if} (x<lt.-10.) \textbf{go} \textbf{to} \textbf{22} \\
\textbf{if} (x<ott.1.5) \textbf{go} \textbf{to} \textbf{4} \\
\textbf{if} (x<lt.-1.5) \textbf{go} \textbf{to} \textbf{4} \\
y=x*(x**3/60.)+(x**9)/3146.+(x**13)/33596. \\
z=(x**3)/3.+(x**7)/42.+(x**11)/1320.+(x**15)/75596. \\
erfc=y-z*x*2.//srt(3.14159) \\
go \textbf{to} \textbf{3} \\
4 \textbf{erfc}=1.--(1.//srt(3.14159)*x*exp(x*x*2)) \\
go \textbf{to} \textbf{3} \\
21 \textbf{erfc}=1. \\
go \textbf{to} \textbf{3} \\
22 \textbf{erfc}=-1. \\
3 return \\
\textbf{end} \\

\textbf{subroutine} \textbf{tit} \\
\textbf{common} \textbf{erfc},tititle(\textbf{A}) \\
\textbf{call} noenc(xp,yo,i) \\
\textbf{call} chaenclity(yo,xhnsait,end) \\
y=yp-2.*y \\
x=0.5*(xp-2.*y) \\
\textbf{call} movto(x,y) \\
\textbf{call} chaarr(tititle,5,4) \\
\textbf{return} \\
\textbf{end}
Fig. A.2.3  
Probe forming system of HB501  
Titchmarsh (1987)
Fig. A 2.4  Signal detection system of HB501
Titchmarsh (1987)
APPENDIX 4

RNO-D (14914)

Chg. 51482

gehärtet: 1075° 30'/Luft

Zugfestigkeit $R_m$ in Abhängigkeit von der Anlaß- und Prüftemperatur
M. Schirra (1984)

Figure A 3.14
Einfluß der Vergütungsbehandlung und Prüftemperatur auf die Zugfestigkeit und 0.2%...-Dehngrenze

M. Schirra (1984)

Probe:
RT: Φ3×39 mm (d₀ × l₀)
200-800: Φ5×25 mm (d₀ × l₀)

Zugfestigkeit $R_m$

0.2-Grenze $R_{P0.2}$

1%-Grenze $R_{P1.0}$

Fig. 3.15
RNO-D (1.4914) Chg. 51482

gehärtet: 1075° 30% Luft

Probe: Ø3·39 mm (d.·lv)

Zugfestigkeit $R_m$ • △ Brucheinschnürung Z
□ Bruchdehnung A
× Gleichmaßdehnung $A_g$

$[\text{MPa}]$

ANLASSTEMPERATUR [°C]  Ageing temperature
APPENDIX 5

PLUTO LITTLE S/P 650/7 86

PLUTO 15.50 HRS. 4/6/87 TO 18.00 HRS. 28/6/87

<table>
<thead>
<tr>
<th>IRRADIATION</th>
<th>15.50</th>
<th>4/6/87</th>
<th>0.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.00</td>
<td>15.50</td>
<td>6/6/87</td>
<td>25.50</td>
</tr>
<tr>
<td>16.00</td>
<td>17.00</td>
<td>6/6/87</td>
<td>0.0</td>
</tr>
<tr>
<td>16.00</td>
<td>28.00</td>
<td>6/6/87</td>
<td>25.50</td>
</tr>
</tbody>
</table>

TOTAL MH. HRS. = 13379.0

IRRADIATION TIME IN SECS = 1.88880E 06

AVERAGE POWER = 25.5

\[ R = 0.0800 \]

SELF-SHIELDING FACTOR = 0.9250

<table>
<thead>
<tr>
<th>MONITOR</th>
<th>INTEGRATED FLUXES</th>
<th>AVERAGE FLUXES</th>
<th>( \phi \text{Fission} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15564</td>
<td>3.478E-20</td>
<td>1.011E 20</td>
<td>1.842E 14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.351E 13</td>
</tr>
<tr>
<td>15565</td>
<td>3.478E-20</td>
<td>1.231E 20</td>
<td>1.842E 14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.519E 13</td>
</tr>
<tr>
<td>15566</td>
<td>3.478E-20</td>
<td>1.117E 20</td>
<td>1.842E 14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.912E 13</td>
</tr>
</tbody>
</table>

COMPUTATION ON 11/09/87