RADIATION EFFECTS AT GRAIN BOUNDARIES

by

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A THESIS SUBMITTED TO THE UNIVERSITY OF SURREY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

SEPTEMBER 1983

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Transmission electron microscopy (TEM) was used to study the effects of ion-irradiation at grain boundaries in a single phase austenitic alloy (Fe,15%Cr,15%Ni) with particular reference to the nucleation and growth of helium gas bubbles. The Harwell Dual Beam Facility was used to implant helium-ions at high temperatures (450° to 600°C). Simultaneous implantation of chromium-ions was used to study the synergistic effects of helium implantation and displacement damage on the development of the radiation induced microstructures. TEM showed that all interfaces except coherent twin interfaces exhibit preferential nucleation of helium bubbles. The density of bubbles at grain boundaries increased with gas implantation rate, decreased slightly with temperature but was independent of extra displacement damage during dual-beam irradiation. The presence of resolvable arrays of grain boundary dislocations at interfaces enhanced the density of helium bubbles at all temperatures studied. A nucleation model was developed to account for the observed density of bubbles at grain boundaries and at grain boundary dislocations. The model was used to show that helium diffusion at grain boundaries and along grain boundary dislocations is slow relative to helium-interstitial migration within grains. Two forms of heterogeneous dislocation loop nucleation were identified at grain boundaries. First, interstitial dislocation loops were observed at coherent twin interfaces. The loop shape was dependent on irradiation conditions and was interpreted in terms of the relative rates of diffusion of interstitial atoms at the twin interface and along the dislocation line. The second form of heterogeneous loop nucleation occurred in the vicinity of some grain boundaries and is consistent with the de-channelling of ions at crystal interfaces.
ACKNOWLEDGEMENTS

I would first like to thank Dr. P. J. Goodhew for supervision of this work. I am grateful for his encouragement and for many helpful discussions and comments (a little caustic wit goes a long way!). Many thanks also to Dr. J. H. Evans for his help at Harwell and for his infectious enthusiasm for research work.

I am grateful to Dr. A. P. Mio downik for use of laboratory facilities. The staff of the MSSU deserve much credit and I particularly wish to thank Dawn and Vernon.

Thanks should also go to Dr. K. M. Knowles whose help with the structure of interfaces was invaluable.

I am indebted to the staff of the Nuclear Physics Division at Harwell. In particular I am grateful for the help of Tony, Mike and Ray who operated the Cockroft-Walton Accelerator.

I wish to thank the SERC and UKAEA Culham for financial support.

Finally, I wish to thank Shirley for her patience, support and encouragement throughout this work; in return, I dedicate this thesis to you.
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CHAPTER ONE. THE MATERIALS PROBLEM OF THE FUSION REACTOR FIRST WALL

1.1 INTRODUCTION

The world's energy requirements can, in the short term, be met by coal, oil and nuclear fission. As sources of fuel diminish (in 50-100 years time(1)) other energy options will be needed. Fusion power is a long term energy option with the potential of cheap and abundant fuel and low radiological hazard (2). The objective of fusion research is to develop the means of creating and controlling matter at very high temperatures, sufficiently high to allow thermonuclear reactions to proceed and produce energy for electricity generation (3). Fusion research has brought us near to the production of a self-sustaining plasma and nearer to the plasma conditions needed in a reactor (2,3). The successful operation of major magnetic fusion devices may demonstrate the scientific feasibility of fusion in the late 1980's (4). Successes in the field of plasma physics have already stimulated research into fusion technology where it is necessary to establish engineering feasibility (2,4,5). For long term reactor operation it is necessary to solve the problem of radiation damage to the first structural wall. Here, the materials problems of the first wall are considered. Particular emphasis is given to helium embrittlement of stainless steel, a major candidate material for the first wall of early fusion devices.

1.2 THE MATERIALS PROBLEM OF THE FIRST WALL

The major materials problem in the development of fusion power is that of the first structural wall (6); the wall that directly faces
the plasma. The first wall (blanket) will be subjected to a severe environment (figure 1.1 after(7)) but must maintain both structural and vacuum integrity. Basic fusion reactions of near term interest are based on the deuterium-tritium (DT) cycle (1-4) and can be written:

\[ _2^4\text{H(D)} + _3^7\text{H(T)} = _4^8\text{He} + _1^1\text{n} \]

Energy is released as the kinetic energy of both the alpha-particle and the neutron. Deuterium is readily separated from water but tritium does not occur naturally and must be generated within the reactor by reactions involving lithium:

\[ ^6\text{Li} + _1^1\text{n} = _3^7\text{T} + _4^8\text{He} + 4.86\text{MeV} \]

\[ ^7\text{Li} + _1^1\text{n} = _3^7\text{T} + _4^8\text{He} + _1^1\text{n} - 2.87\text{MeV} \]

It is envisaged that lithium will be present in the blanket region surrounding the plasma. The blanket also acts to absorb the 14.1MeV neutrons thereby converting the kinetic energy to heat. Plasma temperatures needed for successful reactor operation are of the order of 10^8K (3), so no direct contact between the plasma and any containment vessel can be contemplated. Two containment concepts have evolved; magnetic confinement and inertial confinement and a variety of reactor designs have evolved (5). Magnetic confinement, and more specifically the Tokamak design, has shown most promise to date where the trajectory of the plasma is contained by magnetic fields. The Tokamak design employs a toroidal geometry in which the magnetic field lines close on themselves so direct plasma contact with the wall is inhibited.

The nature of the DT fusion process requires that essentially all of the energy generated passes through the first wall either in the form of energetic neutrons or as heat generated by the deposition of
photons, charged particles or neutral atoms. The fusion neutron spectrum is characterised by a high energy $14.1\text{MeV}$ peak, generated directly by the DT reaction. Approximately 20% of the neutrons in the spectrum are in this high energy tail. These energetic neutrons will generate hydrogen and helium through transmutation reactions within the material of the first wall. The neutron flux through the first wall will also create atomic displacement damage. A $14.1\text{MeV}$ neutron wall loading of $1\text{MWm}^{-2}$ will lead to a displacement rate of about 10 dpa per year (dpa = displacements per atom) in alloys proposed for first wall applications (table 1.1 after (8)). Furthermore, helium will be generated at a rate of hundreds of parts per million per year (8). The high generation rates of helium are expected to cause both swelling, by the formation of bubbles and voids, and embrittlement, by the nucleation and growth of helium bubbles at grain boundaries.

<table>
<thead>
<tr>
<th>METAL/ALLOY</th>
<th>dpa</th>
<th>appmH</th>
<th>appmHe</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminium</td>
<td>14</td>
<td>296</td>
<td>316</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>16</td>
<td>175</td>
<td>142</td>
</tr>
<tr>
<td>ferritic steel</td>
<td>11</td>
<td>450</td>
<td>110</td>
</tr>
<tr>
<td>316 stainless steel</td>
<td>11</td>
<td>532</td>
<td>147</td>
</tr>
<tr>
<td>nickel base alloy (PE16)</td>
<td>12</td>
<td>780</td>
<td>240</td>
</tr>
<tr>
<td>V-15Cr-5Ti</td>
<td>11</td>
<td>245</td>
<td>47</td>
</tr>
<tr>
<td>niobium</td>
<td>7</td>
<td>105</td>
<td>29</td>
</tr>
</tbody>
</table>

The choice of material for the first wall is not solely dependent on the response to neutron irradiation; other factors must be considered. These include compatibility with coolants and with tritium, mechanical and thermal properties, ease of fabrication, cost and long-lived radioactivity (9); no one material is favoured overall.
and the final choice will depend on the objectives of the reactor design. Thermal properties are of particular importance. The upper limit of the wall loading is set by thermal stress considerations (6) and this limit is as low as 2-3 MWm$^{-2}$ for 316 stainless steel but as high as 10 MWm$^{-2}$ for a V-20Ti alloy.

Early fusion reactor designs specified refractory metals as first wall materials on the basis of good thermal efficiency. Recently, the trend has been to specify austenitic stainless steels, which are the only well characterised materials with respect to neutron radiation damage because of experience in existing fission reactors. Stainless steels are also compatible with coolants and with tritium, have adequate mechanical properties, there is an existing joining and fabrication technology and have the advantages of low cost and availability. The lifetime of a stainless steel first wall will be adequate due to the low irradiation exposures expected in early fusion reactors and its use will allow the early demonstration of the scientific and engineering feasibility of fusion power.

1.3 HELIUM EMBRITTLEMENT OF STAINLESS STEELS.

The problem of embrittlement of metals due to neutron irradiation is well known; Barnes (10) first suggested that the effect was due to helium precipitation into bubbles at grain boundaries. Irradiation induced embrittlement in austenitic stainless steels irradiated at elevated temperatures was first demonstrated in the mid-60's (11). Exposure of stainless steels to high neutron fluences in fast reactors results in additional embrittlement at intermediate temperatures (12,13). High temperature embrittlement has been studied using both
reactor irradiated (11,14-17) and helium-implanted (18-23) specimens. Generally, creep ductility is reduced and intergranular failure is enhanced. The effects of irradiation on rupture time are not simple; significant differences exist between results from in-situ and post-irradiation creep tests (12,24). High concentrations of transmutant helium lead to a significant increase in the number of creep cavities which appear to form on pre-existing helium bubbles at grain boundaries (19,20,25).

A number of models have been developed to describe the role of helium in high temperature embrittlement during post-irradiation creep tests (24-27) and during "in-reactor" creep tests (25,28). A central feature of all the embrittlement models is that creep cavities nucleate on radiation induced helium bubbles. All of the models point to the severe embrittlement which can be expected in the first wall of fusion reactors due to high generation rates of helium.

At low temperatures, irradiation induced matrix strengthening by cavities (bubbles or voids) and dislocation loops may facilitate crack nucleation and unstable crack propagation (12). Furthermore, helium may enhance elemental segregation to grain boundaries (29,30) which can contribute to embrittlement. The presence of atomic helium at grain boundaries may also aid the nucleation of wedge cracks (29). The contribution of these additional mechanisms to the overall embrittlement is not clear. The first wall of a fusion reactor will necessarily operate at elevated temperatures where helium bubbles, as nuclei for creep cavities, are likely to be the dominant source of embrittlement.
First wall materials of fusion reactors will be exposed to a severe radiation environment. High energy neutrons will generate high levels of helium and will cause displacement damage. Helium will diffuse to grain boundaries and may lead to embrittlement either as atomic helium by aiding critical crack nucleation or as helium bubbles. Experimental evidence and theoretical treatments suggest that the high generation rates of helium gas will set a severe restriction on the useful lifetime of first wall materials. The characteristics of helium bubble nucleation and growth at grain boundaries must be appreciated to understand and overcome the embrittlement problem.
2.1 INTRODUCTION

Helium gas will be generated by transmutation reactions in the first wall of a fusion reactor. Helium is effectively insoluble in metals and diffusion of helium will lead to entrapment at vacancies, gas atom-vacancy clusters, dislocations and grain boundaries. The relative strengths of these trapping sites (i.e. binding energies) will control the microstructural distribution of helium. An understanding of the diffusion mechanisms and of the relative helium-defect binding energies will lead to an appreciation of the microstructural redistribution of helium in first wall materials. This chapter describes the theoretical models and physical evidence for the properties of atomic helium in metals.

2.2 HELIUM TRAPPING AT LATTICE DEFECTS

In the absence of an experimental technique to characterise sub-microscopic helium-defect interactions it has been necessary to turn to theoretical modelling. Crystal processes can be simulated using an atomic model of the lattice. The equations of motion are computed for each atom as the lattice is subjected to an external stimulus such as the introduction of a helium atom. Early calculations by Rimmer and Cottrell (31) for the inert gases in copper showed that all rare gas atoms prefer to occupy a substitutional site whenever vacancies are available. The larger inert gas atoms can generate a Frenkel defect and are able to move easily from an interstitial site to a substitutional one. However, helium is not
able to do so and resides interstitially when vacancies are not available. Melius, Wilson and Bisson (32) recently calculated substitutional formation energies for the rare gas atoms in nickel and found the same trends as Rimmer and Cottrell found for copper. The formation energies of interstitial and substitutional helium are shown in Table 2.1. The binding energy of helium to a vacancy is also shown as the difference between the two formation energies. A vacancy represents a significant trap for a helium atom.

<table>
<thead>
<tr>
<th>METAL*</th>
<th>ENERGY(eV)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>FORMATION ENERGY</td>
<td>Ni</td>
<td>2.67</td>
</tr>
<tr>
<td>Interstitial helium</td>
<td>Ni</td>
<td>0.18</td>
</tr>
<tr>
<td>Substitutional helium</td>
<td>Ni</td>
<td>2.49</td>
</tr>
<tr>
<td>Helium-vacancy</td>
<td>W</td>
<td>1.53</td>
</tr>
<tr>
<td>Helium-dislocation</td>
<td>Mo</td>
<td>1.55</td>
</tr>
<tr>
<td>Helium-dislocation</td>
<td>Fe</td>
<td>2.10</td>
</tr>
<tr>
<td>Helium-dislocation</td>
<td>-</td>
<td>2.67approx.</td>
</tr>
<tr>
<td>Helium-grain boundary</td>
<td>Ni</td>
<td>1.07</td>
</tr>
<tr>
<td>BINDING ENERGY</td>
<td>Ni</td>
<td>1.35</td>
</tr>
<tr>
<td>Helium-divacancy complex</td>
<td>Ni</td>
<td>1.35</td>
</tr>
<tr>
<td>Interstitial helium at a dislocation</td>
<td>W/Mo</td>
<td>0.3-0.4</td>
</tr>
</tbody>
</table>

* Where possible, values for nickel are tabulated. To a first approximation the properties of helium in nickel reflect the properties in austenitic steels.
Impurity atoms act as alternative trapping sites for helium. Kornelsen and van Gorkum (33) studied the trapping of helium in tungsten pre-implanted with He, Ne, Ar, Kr and Xe. They proposed that helium was significantly bound to the rare-gas atom defects. It was recently suggested that compositional differences in alloys may effect the mechanism of helium clustering (34). One possible mechanism proposed was a size effect, where solute atoms of markedly different sizes provide strain fields that act as favourable trapping sites for helium. In the absence of additional evidence it is difficult to estimate the contribution of solute atoms to the overall entrapment of helium.

Dislocations are important trapping sites for helium atoms. The interaction of helium atoms with dislocations must be appreciated because dislocations are a dominant feature of irradiation induced microstructures. The elastic interaction between impurity atoms and an edge dislocation can result in significant increases in solute concentration along the dislocation line (35). The concentration of solute atoms, $C_d$, at a dislocation is related to the average concentration, $C_0$, by the expression:

$$C_d = C_0 \exp(-U/kT)$$

Where $U$ is the binding energy of a solute atom to a dislocation, $k$ the Boltzman's constant and $T$ is the absolute temperature. The binding energy $U$ between a solute atom and the strain field of a dislocation is given by (35):

$$U = \frac{4Gbr^2E_m\sin\theta}{R} \quad \ldots \ldots 2.1$$

Where $G$ is the shear modulus, $b$ the Burgers vector of the dislocation, $r$ is the atomic radius, $R$ is the distance of the solute atom from the
dislocation and $\theta$ is the angle between the slip plane and the
direction of $R$. The misfit parameter $E_m$ is defined as:

$$E_m = \frac{(r_s - r_a)}{r_a}$$

where $r_s$ and $r_a$ are the radii of the solute and the parent
atoms respectively. Helium, being a small atom has a negative misfit
parameter and is attracted to the compressive side of the dislocation
(36). This model for binding of helium atoms to a dislocation is
inappropriate for the binding of gas atoms at the dislocation core,
where equation 2.1 does not apply.

The interaction of helium atoms with the core of edge
dislocations has recently been considered using an atomistic approach
(37,38). The binding energy of a helium atom to a perfect
$1/2<111>(110)$ edge dislocation was calculated for the BCC metals
tungsten (37), molybdenum (37) and iron (38). The calculations showed
that the helium atom is bound nearly twice as strongly at a vacancy
than at a dislocation (table 2.1). In addition, the migration energy
along the dislocation did not differ appreciably from that for
interstitial migration in the bulk. Thus, a straight edge dislocation
acts as a trap for helium but the gas retains considerable mobility
along the dislocation core. In reality, edge dislocations are not
perfectly straight but contain jogs and kinks. Reed argues (39) that
a helium atom will behave in much the same way as a self-interstitial
atom in that it will encounter a jog and occupy the site with
virtually no formation energy. The atom will be bound by an energy
equivalent to the interstitial formation energy. The jogged
dislocation is, therefore, a strong trap for atomic helium, which is
stable against thermal detrapping. The gas atom is trapped in the
dislocation core by elastic interactions but is free to migrate along
the core until it encounters a jog, where it is strongly bound.

Although not strictly a lattice defect, grain boundaries are a significant trapping site for helium. The trapping of helium at grain boundaries can lead to the nucleation and growth of gas bubbles which are the source of the helium embrittlement problem (Chapter 1). Despite the technological demand for a solution to the embrittlement problem our understanding of the properties of helium at grain boundaries is poor. Little is known about the diffusion of small interstitial atoms at grain boundaries (40); this is an obstacle to the successful modelling of helium embrittlement (41). Recently, Baskes and Vitek used computer modelling to calculate the binding energy of hydrogen and helium at various sites in a $\Sigma_{11}$ boundary in nickel (42). The binding energy of helium at specific sites in the interface was as high as 1.07 eV. Helium was found to behave as an interstitial even in the boundary where there was a strong dilatational field around it. This is the first theoretical evidence for strong trapping sites in an interface. The binding energy at alternative sites in the interface was as low as 0.09 eV.

2.3 MIGRATION OF HELIUM

Helium atoms may reside interstitially in the lattice or in vacancies as substitutional atoms. Furthermore, helium atoms are readily trapped at dislocations and grain boundaries. The migration of helium in metals is made complicated by interactions with these defects and we can expect temperature and radiation to be important factors in the diffusion mechanism. Ghoniem and Takata (43) recently identified the factors which contribute to the complex migration
behaviour of helium:
1. Trapping/detrapping in single vacancies, di-vacancies and higher order vacancy complexes.
2. Trapping at dislocations and grain boundaries.
3. Replacement of substitutional helium with self-interstitials.
4. Clustering with other vacancies and helium.
5. Resolution from traps by irradiation.
6. Migration as an interstitial, substitutional or di-vacancy complex.

Due to the complexity of helium migration it is difficult to determine reliable diffusion data. Helium has a low solubility in metals which requires that it is introduced by implantation or by nuclear reactions, which generally introduce Frenkel defects. Consequently, the diffusion of helium may be affected by the experimentally introduced defects. Semi-quantitative techniques have evolved which indicate that helium can diffuse very rapidly in a metal. Mono-energetic ions have been implanted into metals and the resultant helium depth distribution was investigated by nuclear methods as a function of temperature (44,45). The change in the helium distribution indicated a rapid diffusion rate. Helium can be introduced into a metal without producing Frenkel defects by implantation with energies below that for defect production. Alternatively, tritium can be dissolved in the metal and radioactive decay produces helium ($^3$He)(46-48). The subsequent release of helium at low temperatures indicated a rapid diffusion mechanism but again it was not possible to measure the diffusion coefficient reliably.

Phillips et al (49) recently used high energy implantation of
nickel to study helium diffusion. At the high temperatures used (>1023K) the influence of radiation-produced defects was negligible and it was possible to determine the diffusion coefficient of helium in the presence of thermal vacancies. High temperature helium implantation was used and from measurements of the time dependence of the helium release during implantation it was possible to determine the diffusion coefficient. The activation energy of 0.81 eV and the pre-exponential factor of $6 \times 10^{-7} \text{m}^2\text{s}^{-1}$ were consistent with a model in which the helium diffuses interstitially between thermal vacancies where it is trapped and subsequently released by thermal activation.

In the absence of definitive experimental results it has been necessary to turn to theoretical modelling to characterise helium migration in metals. Two approaches have evolved; atomistic modelling has been used to calculate the migration energy of interstitial and substitutional helium and of helium-vacancy complexes. Alternatively, rate-theory has been used to determine the dominant diffusion mechanisms during irradiation. Wilson and Johnson first used an atomistic approach to calculate the migration energies of interstitial helium in a variety of FCC and BCC metals (50). Generally, the helium interstitial migration energy in BCC metals was typically 0.2 eV, whereas in the FCC metals values were less consistent ranging from 0.08 eV for nickel to 1.74 eV in palladium. In a more detailed study, Wilson and Bisson calculated an interstitial migration energy of 0.45 eV for helium in copper (51) whereas a value of 0.57 eV was previously reported. Wilson and Bisson also presented a model for the combined migration of a helium atom and a vacancy where the helium atom would move to an interstitial position, a metal atom would move
into the vacancy so produced, leaving the helium atom to fall into the new vacant site.

Melius et al (32,52,53) variously report the interstitial migration energy of helium in nickel in the range 0.43-0.83eV as calculated using an atomistic approach (table 2.1). The calculated migration energy is sensitive to the chosen interatomic potentials and Melius et al give 0.4-0.5 as a reasonable estimate of the actual migration energy (32). Migration of substitutional helium was found to be unlikely because break up of the helium-vacancy complex was energetically favoured over migration. Thus, substitutional helium is essentially immobile (32). The atomistic calculations of Melius et al also show that a helium-divacancy complex is highly mobile with a migration energy of 1.35eV. The migration mechanism proposed involves the jump of a nearest neighbour lattice atom into the empty vacancy, after which the helium atom jumps into the newly formed vacancy (32).

Atomistic calculations show that helium diffuses rapidly as an interstitial atom but is effectively immobile as a substitutional atom. Also, a helium divacancy complex is highly mobile. Rate theory has been used to predict which of these migration mechanisms will control helium transport during irradiation since it is not clear which mechanism will operate in the presence of radiation induced point defects. Kinetic rate theory models the dynamic interactions of mobile helium with vacancies, interstitials, vacancy clusters and dislocations (43,54-59). The calculations involve the solution of a series of rate equations and a number of general conclusions can be drawn related to the migration mechanisms of helium during irradiation:
1. There is a significant binding energy between a helium atom and a vacancy but the complex is unstable against detrapping. Interstitial knock-out is the dominant detrapping mechanism up to a temperature of 873K. Radiation induced detrapping and thermal detrapping do not contribute significantly to the release of helium atoms from vacancies at temperatures <873K (56,58).

2. He$_6$V complexes (six helium atoms in a vacancy) are readily formed during irradiation and are stable against interstitial knock-out.

3. HeV$_2$ complexes (helium-divacancy) do not make a significant contribution to the transport of helium atoms (58).

Reed (39) proposed a simple diffusion mechanism for helium in the presence of vacancies where helium diffuses as an interstitial atom between the vacancy traps. The effective diffusion coefficient, D, was given by:

$$D = \frac{\nu \lambda^2 \alpha}{6} C_v^{-2/3} \exp\left(-\frac{E_d}{kT}\right)$$

where $\nu$ is the helium vibrational frequency, $\lambda$ is the interatomic jump distance, $C_v$ the vacancy concentration. $E_d$ is the helium detrapping energy and $k$ and $T$ are the Boltzmann's constant and the absolute temperature respectively. Here, the detrapping rate is controlled by thermal activation so it is not clear that this effective diffusion coefficient is appropriate during irradiation.

2.4 SUMMARY

Helium atoms are trapped at vacancies, dislocations and grain boundaries. A substitutional helium atom is effectively immobile but a helium atom at a straight dislocation may retain significant
mobility along the core. Dislocations with jogs and kinks are strong traps for helium but mobility along the core is impaired. Our knowledge of helium trapping at grain boundaries is poor. At high temperatures and/or during irradiation the dominant transport mechanism for helium through a crystal is as an interstitial atom via vacancy traps. Detrapping from vacancies can occur thermally or by replacement with a self-interstitial atom.
3.1 INTRODUCTION

Helium bubbles will contribute to both swelling and embrittlement in fusion reactor first wall materials. In this chapter the nucleation of helium bubbles is first considered. Growth mechanisms of bubbles are also discussed. The microstructural distribution of helium bubbles is also considered with particular emphasis on the interaction of helium bubbles with grain boundaries, dislocations and particle-matrix interfaces.

3.2 NUCLEATION OF HELIUM BUBBLES

A variety of bubble nucleation theories have been developed. Wiedersich and Katz (60) describe nucleation by the condensation of vacancies. The vacancy clusters may collapse into dislocation loops unless stabilised by the presence of gas. In this type of theory it is not clear that gas atoms will reach the vacancy cluster in time to avoid collapse into a loop (61). An alternative theoretical approach is to describe bubble nucleation by the homogeneous agglomeration of gas atoms, rather than vacancies. In this way Greenwood et al (62) proposed a model for bubble nucleation in fissile material. It was assumed that two gas atoms in association with a vacancy form a stable bubble nucleus. The homogeneous nucleation separation was derived by assuming that the number of nuclei increases until there are so many that a newly created gas atom is more likely to reach an existing nucleus than meet another gas atom. The homogeneous nucleation separation $2r_1$ was given by:

\[ 2r_1 = \frac{4\pi N \rho}{S} \]

17
where $D$ is the gas atom diffusion coefficient, $r_0$ is the radius of a bubble nucleus, $a$ is the lattice spacing, $G$ the gas atom generation rate and $z$ is the number of sites explored per gas atom jump. The model was later shown to be consistent with experimental results (63,64).

The possibility of homogeneous gas bubble nucleation was developed further by Singh and Foreman (65,66). In this theory, helium atoms are immobile when trapped in vacancies but become mobile either by the addition of a vacancy (forming a mobile helium-divacancy complex) or by displacement by a self-interstitial atom. The diffusion of detrapped helium produces larger and less mobile vacancy-gas clusters, leading to the formation of bubbles. In a recent nucleation theory Mayer and Brown (61) allow nucleation to occur either by the stabilization of vacancy clusters by gas atoms or by the formation of gas atom pairs (homogeneous gas bubble nucleation). In comparison, Ghoniem and Takata (43) argue that a di-helium cluster is not stable during neutron irradiation due to the possibilities of thermal detrapping and radiation resolution. A tri-helium cluster was assumed to form the critical bubble nucleus.

In contrast to homogeneous bubble nucleation theories outlined above, Hayns and Wood (67) developed a model to describe simultaneous homogeneous and heterogeneous nucleation. Homogeneous nucleation occurred by the formation of di-helium complexes and heterogeneous nucleation was assumed to occur at solute atoms where the binding energy of an interstitial helium atom was of the order of 1eV but was a variable. For large values of binding energy the nucleation was
dominated by the heterogeneous sites whereas small binding energies meant that the trapping centres were not stable against thermal detrapping and nucleation was homogeneous. As recently discussed by Singh and Foreman (66) nucleation theories are inadequate in that they do not fully reflect experimental observation. In particular, the diffusion mechanism for helium during irradiation is poorly understood and is a major obstacle in modelling the nucleation of gas bubbles and voids.

The homogeneous nucleation models outlined above are based on the assumption that bubble nucleation is dictated by the properties of helium atoms rather than by vacancies. This is largely substantiated by experiment. Helium bubbles nucleate and grow during implantation at low temperatures \( (T < 0.3T_m) \) where vacancies are effectively immobile. Bubbles nucleate during room temperature implantation of molybdenum (68), stainless steel (69), nickel (69), and copper (70). Since the nucleation of gas bubbles requires both vacancies and gas atoms it is necessary to consider bubble nucleation mechanisms which are independent of vacancy mobility. Thermal helium desorption spectroscopy (THDS), coupled with lattice relaxation calculations have led to a recent model for helium bubble nucleation at low temperatures (71).

THDS involves implantation of helium ions into a target metal at energies of a few eV to a few MeV. The helium release spectrum is recorded during post bombardment annealing and deductions can often be made about the nature of rare-gas diffusion and of the properties of helium-vacancy complexes. Reed reviewed the results from early THDS experiments (39). Kornelsen (72) recorded the desorption spectra from
tungsten and showed:
1. Helium entrapment increases considerably when a metal is pre-damaged by ion irradiation. Trapping is low when helium is implanted at sub-threshold levels.
2. Helium release-peaks can be associated with the binding energy of helium in vacancies.
3. Vacancies can be occupied by at least four helium atoms.

The results of Kornelsen (72) were largely substantiated by atomistic calculations (73,74)(see Table 3.1). In addition, Wilson and Bisson (73) calculated that up to six helium atoms in an octahedral configuration could be accommodated by a single vacancy whilst up to thirty helium atoms could be associated with the strain field of a vacancy.

<table>
<thead>
<tr>
<th>EXPERIMENTAL HELIUM RELEASE REACTION (80)</th>
<th>EXPERIMENTAL ACTIVATION ENERGY (80)</th>
<th>THEORETICAL ACTIVATION ENERGY (81)</th>
<th>THEORETICAL ACTIVATION ENERGY (82)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He V $\rightarrow$ He + He V$_3$</td>
<td>2.41eV</td>
<td>2.50eV</td>
<td>2.94eV</td>
</tr>
<tr>
<td>1120K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He V $\rightarrow$ He + He V$_2$</td>
<td>2.88eV</td>
<td>2.52eV</td>
<td>3.02eV</td>
</tr>
<tr>
<td>1220K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He V $\rightarrow$ He + He V</td>
<td>3.14eV</td>
<td>2.89eV</td>
<td>3.43eV</td>
</tr>
<tr>
<td>1480K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>He V $\rightarrow$ He + V</td>
<td>4.05eV</td>
<td>4.40eV</td>
<td>5.07eV</td>
</tr>
</tbody>
</table>

Further atomistic calculations for BCC molybdenum and FCC copper (75) also show that multiple levels of vacancy occupation are
possible. This is a major feature of a recent model for low temperature bubble nucleation (71). The model is based on the following observations:

1. At low temperatures, vacancies and vacancy clusters are immobile but self interstitial atoms and interstitial helium atoms are mobile.

2. Vacancies trap helium atoms to form \( \text{He}_nV \) (\( n=1 \) to 6).

3. \( \text{He}_6V \) clusters can capture more interstitial helium atoms. The binding energy of an additional number of helium atoms (about 4) is comparable to that of the sixth helium atom (32). By adding more interstitial helium atoms to the complex higher helium binding energies are found (33). This observation has been interpreted in terms of 'trap-mutation' whereby the cluster generates a second vacancy by emitting a self-interstitial atom. The increased binding energies are thus associated with a divacancy complex. As more helium atoms are added the trapped fraction of the implanted low energy helium increases indicating that the trap effectiveness increases continuously with helium content.

4. It it most likely that at some size the helium filled vacancy cluster punches out an interstitial dislocation loop rather than a series of single interstitials.

5. Self interstitial atoms annihilate the vacancy of a \( \text{He}_nV \) (\( n<5 \)) and produces interstitial helium atoms. \( \text{He}_mV_2 \)'s and larger clusters formed by mutation cannot be annihilated by self interstitial atoms.

Using a Monte Carlo procedure Baskes et al (71) described the nucleation and growth of helium bubbles based on the development of helium-vacancy clusters as outlined above. Theory was found to describe the nucleation density and size of helium bubbles as observed
experimentally. An important feature of the model is that clusters grow by generating self-interstitial atoms which are emitted as interstitial dislocation loops. Caspers et al recently used lattice relaxation calculations to study the trap-mutation process in BCC iron (76). Self interstitials were not emitted as single atoms due to a significant binding interaction between a self-interstitial and a helium-vacancy cluster. The loop punching model for the growth of small overpressurized bubbles is based on the early work of Greenwood et al (62) and is considered in the next section.

Recently, Evans et al (77) and van Veen et al (78) have identified an alternative mechanism for gas bubble nucleation at low temperatures. They observed the formation of two-dimensional (110) helium platelets in molybdenum during irradiation with helium ions at an energy below the threshold energy for displacement damage. The platelets form on pre-existing He-V nuclei introduced by a previous implantation. On subsequent annealing each platelet transforms to a few small helium bubbles, a process which was later analysed by Tyler and Goodhew (79). It is not clear what contribution the platelets make to the nucleation of helium bubbles during high temperature irradiation.

In summary, there is a substantial amount of experimental and theoretical work which indicates that gas bubble nucleation can occur at temperatures where vacancies are immobile. This evidence lends support to nucleation theories based on the agglomeration of gas atoms rather than vacancies. Single vacancies are effectively unsaturable traps for helium atoms due to the process of trap mutation whereby vacancies are generated by the emission of interstitial atoms.
Experimental evidence for gas bubble nucleation at high temperatures, where vacancies are mobile, is limited. Presumably, gas atom agglomeration dominates the bubble nucleation process in this regime but it is not clear that trap-mutation is necessary because vacancies are mobile and available to relieve the overpressure in small bubbles.

3.3 GROWTH OF HELIUM GAS BUBBLES

Inert gas bubbles can, in principle, grow by one or all of three mechanisms (80):

1. Continuous gas atom and vacancy supply.
2. Growth by redissolved gas atoms and vacancies from shrinking bubbles.
3. Migration and coalescence.

The first mechanism can only operate when gas is implanted or generated by transmutation reactions. Ostwald ripening (the second mechanism) may occur during irradiation (81) but is unlikely in the absence of displacement damage because of the low solubility of inert gas atoms in metals (31,36). Migration and coalescence occurs at elevated temperatures and is the operative growth mechanism in the absence of irradiation in a variety of FCC (82,83) and BCC (83,84) metals.

3.3.1 BUBBLE GROWTH MECHANISMS DURING IRRADIATION.

Irradiation produces a supersaturation of self-interstitial atoms and vacancies and helium may be implanted or generated by transmutation reactions. Consequently, bubble growth is a function of
the flux of gas atoms, vacancies and interstitials to the bubbles. At low temperatures vacancies are immobile, yet helium bubbles do nucleate and grow (section 3.2). Greenwood et al (62) first proposed that overpressurized bubbles can grow by a mechanism of loop punching. Vacancies are created to relieve the pressure by punching out a platelet of interstitial atoms along a glide plane. The required pressure, \( P \), to drive the process is:

\[
P \geq 2\frac{Y}{r} + Gb\log_e(r/b) \tag{3.1}
\]

Where \( P \), \( r \) and \( Y \) are the pressure, radius and surface energy of the bubble, \( G \) is the shear modulus and \( b \) is the Burgers vector of the resulting dislocation loop.

Direct experimental observations support the loop punching model. Wampler et al (85) observed loop punching using TEM of copper foils quenched from hydrogen atmospheres where the excess hydrogen precipitates as bubbles. Shiraishi et al (86) present results which indicate that the flux of self-interstitials into bubbles is sufficient to increase the bubble pressure and cause loop punching. More recently, Evans et al (87) have presented direct evidence for helium bubble growth in molybdenum by loop punching. Helium was initially implanted at 3keV, essentially to nucleate bubbles. Subsequent helium implantation at 150eV allowed some of the helium to reach the bubble nuclei in the absence of displacement damage. TEM of the implanted foils showed aligned dislocation loops emanating from the bubbles.

Evans et al (87) argue that the loop punching mechanism for bubble growth must still apply during conventional helium implantation, at least at temperatures where vacancies are immobile.
Loop punching could take place both to accommodate the arrival of helium at bubbles and to compensate for the flux of self-interstitial atoms. Furthermore, at higher temperatures the conventional (bias-driven) void growth mechanism may allow a net flux of vacancies to bubbles. The overpressure in a bubble would then be a function of the relative fluxes of vacancies and gas atoms into a bubble. Recent experimental evidence of the growth of helium bubbles in nickel is consistent with the loop punching model over the temperature range 200K-600K (88).

Electron irradiation causes bubble growth in copper previously implanted with 30KeV helium ions at 300K (89) and also in 5KeV helium implanted nickel at 273K (90). Johnson and Mazey proposed a number of possible growth mechanisms:
1. Processes involving the detrapping of helium from HeV clusters.
2. Radiation assisted migration of helium.
4. Athermal radiation assisted migration of vacancies.

Swygenhoven et al (90) argue that bubble growth by vacancy absorption is unlikely during 1MeV electron irradiation; rather, a significant amount of helium resides outside the bubbles (probably in helium-vacancy clusters) and irradiation induced detrapping releases helium from the clusters which diffuses to the bubbles and causes growth by loop punching.

Resolution of helium from bubbles is normally considered unlikely due to the very low solubility of helium in metals. However, Ostwald ripening may contribute to bubble growth during irradiation. Gas
diffusion controlled growth results from resolution and is important in nuclear fuels. Whapham (91) suggested that the local heating caused by a fission fragment could lead to the explosive destruction of a bubble. Nelson (81) proposed that the gas is redissolved by sputtering when an atomic projectile collides with the bubble. The resultant supersaturated solution of gas can precipitate during subsequent annealing as bubbles whose growth is limited by gas atom diffusion. There is little experimental evidence to support the resolution mechanism in metals. Nelson argues that, in comparison to a fission fragment, a primary knock-on atom in a metal creates little lattice disturbance and the resolution process will be less efficient in metals. In a recent rate theory for swelling of fusion materials Ghoniem and Takata (43) calculate that the dispersion of helium atoms by resolution from bubbles is a significant process in metals especially at low temperatures.

3.3.2 BUBBLE GROWTH DURING ANNEALING

During annealing experiments there is no gas supply to bubbles, consequently bubble growth is limited to migration and coalescence. Lidiard and Nelson (92) predict a short range attraction between bubbles which ensures that coalescence occurs. Experimentally, Barnes and Mazey (82) and Tyler and Goodhew (80) have shown that helium bubble coalescence is particularly rapid. The rate controlling step for bubble growth is migration which, in the absence of any external driving force, is by Brownian motion (93). Temperature and stress gradients impose a directional drift velocity on random migration processes (82,94-96). The random migration of a bubble requires the transfer of atoms from the leading surface to the trailing surface and
a number of mechanisms may control the rate of atom transfer. Atoms may diffuse through the bubble by vapour transport, around a bubble surface by surface diffusion or through the surrounding metal by volume transport. Shewmon predicted that surface diffusion will control the migration of small bubbles (<1 \mu m)(95).

An additional process may limit bubble migration; bubbles are frequently faceted and it is necessary to nucleate ledges on the facets to allow bubble migration (97). The four possible mechanisms which can control the migration rate of helium bubbles are vapour diffusion, surface diffusion, volume diffusion and ledge nucleation. For each mechanism, the bubble diffusion coefficient is a function of bubble size and the size dependence is different for each transport mechanism (80,83). Furthermore, the size dependence is a function of the assumed pressure change on coalescence(80). For growth kinetics of bubbles at relatively high temperatures it is generally assumed that bubbles maintain an equilibrium pressure after coalescence (94). However, Goodhew and Tyler (80) have shown that this assumption is not valid at temperatures below about 0.5T_m. When bubbles coalesce the resultant bubble does not rapidly attain equilibrium because the supply of thermal vacancies is limited; constant pressure is maintained. If the bubbles maintain an equilibrium pressure it is possible to differentiate between the rate controlling mechanisms from the time dependence of the mean bubble size (Table 3.2). At lower temperatures this time dependence does not give a clear distinction between vapour, volume and surface controlled migration (Table 3.2)(80).
A variety of migration mechanisms have been reported in the literature for helium bubbles in stainless steels. Migration of large faceted bubbles ($r>10$nm) in 316 stainless steel at 1023K was controlled by ledge nucleation; whereas, for smaller bubbles, at lower temperatures migration was consistent with a volume diffusion mechanism (98). Walker similarly reported volume diffusion control of bubble migration in a 20\%Cr, 25\%Ni, Nb-stabilised austenitic alloy (99). Braski et al (100) report a similar volume diffusion controlled growth mechanism for helium bubbles in a 17\%Cr, 17\%Ni austenitic steel. In contrast, Smidt and Pieper (83, 101) report bubble migration controlled by surface diffusion in 316 stainless steel during annealing at 873K-1373K. Rothaut and Schroeder (102) report growth kinetics controlled by vapour transport of atoms across bubbles. They also reported a high activation energy for bubble diffusion of 3.8eV and on this basis proposed Ostwald ripening as the growth mechanism. Armstrong and Goodhew (98) report a similarly high activation energy (4.9eV) and argue that bubble size during annealing may be affected by the uptake of thermal vacancies. An anomalously high activation energy for surface controlled bubble migration was also reported for 316 stainless steel (101).
3.4 MICROSTRUCTURAL DISTRIBUTION OF HELIUM BUBBLES

3.4.1. HELIUM BUBBLES AT GRAIN BOUNDARIES

The problem of helium bubbles at grain boundaries has been known for many years. Barnes observed helium bubbles at grain boundaries in copper (103) and studies of inert gas bubbles at grain boundaries in UO$_2$ were driven by the technological impetus to reduce swelling in nuclear fuels (104). Despite the strong technological demand for a solution to helium induced embrittlement in fast-reactor and fusion-reactor structural materials our understanding of the binding, diffusion and clustering of helium atoms at grain boundaries is poor. Evidence for bubble nucleation at grain boundaries is limited to TEM observation of small bubbles.

Braski et al (100) studied the development of grain boundary bubbles in a ternary austenitic alloy (Fe-17%Cr-17%Ni) by annealing pre-irradiated samples at 1023K. Bubble size and density varied considerably from boundary to boundary indicating that misorientation plays a role in a boundary's effectiveness as a nucleation site. The decoration of grain boundary dislocations (GBDs) with helium bubbles was first demonstrated. It was inferred that GBDs act as preferential bubble nucleation sites. Similarly, Kesternich and Rothaut (105) reported a dependence of bubble nucleation density on dislocation spacing in a low angle grain boundary in a commercial stainless steel.

The growth rate of bubbles at grain boundaries is enhanced relative to that of bubbles within grains (100). The enhanced growth rate can be accounted for by restricted two dimensional migration of bubbles at boundaries leading to an enhanced chance of coalescence.
Wolfenden and Farrell (106) estimated the coalescence rate of bubbles within the boundary plane and give the pair-wise coalescence time, $t_c$, as:

$$t_c = \frac{14}{32r^2D_b}$$

Where $l$ is the interbubble spacing, $r$ is the bubble radius and $D_b$ is the bubble diffusion coefficient. Greenwood reports three additional growth mechanisms which, in principle, may apply to helium bubbles at grain boundaries (107):

1. Stress induced growth (see Chapter 1).
2. Ostwald ripening.
3. Bubble sweeping by grain boundary migration.

Ostwald ripening may contribute to bubble growth if there is a finite solubility of helium at the grain boundaries but there is no evidence to support this argument for helium. However, Wolfenden and Farrell report a resolution mechanism for the growth of gas bubbles (a mixture of fluorine, hydrogen, oxygen and nitrogen) at grain boundaries in tungsten (106).

Bubble sweeping by migrating grain boundaries may contribute to bubble growth (107). Speight and Greenwood (108) give the conditions necessary for bubble sweeping when the driving force for boundary motion is equal to the bubble pinning force. For a given driving force for boundary motion a critical size exists for detachment from the boundary and is given by:

$$r^4 = \frac{3a^2f l^2}{8\pi} \exp \left( \frac{Q - Q_s}{kT} \right)$$

Where $a^3$ is the volume of an atom, $l$ the spacing of bubbles in the boundary, $f$ an entropy factor, $Q$ the activation energy for boundary motion and $Q_s$ the activation energy for surface diffusion. A
boundary sweeps bubbles until migration and coalescence within the plane produces bubbles of a critical size, at which they become detached.

If the driving force for boundary migration is larger than the bubble pinning force, the boundary can break away from bubbles (109). Helium bubbles were found to be ineffectual in impeding boundary motion in copper (110) and in gold (111). From these considerations, sweeping is most likely when the driving force for boundary migration is low, as in fully recrystallised metals. However, Maziasz et al (112) report bubble sweeping by advancing austenite boundaries in cold worked stainless steel.

Zones denuded of helium bubbles adjacent to grain boundaries have been reported in the literature. The observation is sensitive to the experimental conditions used. Table 3.3 shows some of the apparently conflicting evidence for the formation of bubble denuded zones. It is difficult to draw any conclusions as to the roles of implantation temperature, post-implantation annealing and helium concentration on the formation of bubble denuded zones because of the range of materials and implantation techniques used.
### TABLE 3.3
Experimental observation of bubble denuded zones at grain boundaries.

<table>
<thead>
<tr>
<th>METAL</th>
<th>REF.</th>
<th>CONDITION</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-10%Cr</td>
<td>113</td>
<td>Triple-beam irradiation (Fe-,He- and H-ions) at 725-950K</td>
<td>Bubble denuded zones reported</td>
</tr>
<tr>
<td>Nimonic PE16 alloy</td>
<td>114</td>
<td>Triple-beam irradiation (Fe-,He and H-ions) at 898K</td>
<td>Narrow denuded zones only 15nm wide were reported</td>
</tr>
<tr>
<td>316 Stainless steel</td>
<td>115</td>
<td>Helium-ion implantation of TEM thin foils at 773-923K</td>
<td>Majority of interfaces exhibited little or no bubble denudation</td>
</tr>
<tr>
<td>Al-Li alloy</td>
<td>116</td>
<td>Neutron-irradiation at 473-873K</td>
<td>No denuded zones apparent at low doses. 750nm wide zones developed at high doses</td>
</tr>
<tr>
<td>Niobium</td>
<td>117</td>
<td>Helium-ion implantation at 1023K or at room temperature followed by annealing</td>
<td>Bubble denuded zones form during high temperature implantation but not after cold implantation/annealing</td>
</tr>
<tr>
<td>Aluminium</td>
<td>118</td>
<td>600MeV proton irradiation at room temperature</td>
<td>Helium bubbles nucleate and grow close to interfaces but not within grains</td>
</tr>
<tr>
<td>Copper</td>
<td>103</td>
<td>Helium-ion implantation followed by annealing</td>
<td>Bubble denuded zones reported</td>
</tr>
</tbody>
</table>

### 3.4.2 HELIUM BUBBLES AT DISLOCATIONS

Helium bubbles have been observed at dislocations in a number of metals and provide indirect evidence for the segregation of helium atoms to dislocations. However, it is difficult to attribute the observation to preferred bubble nucleation since both bubble migration and dislocation motion are possible during long annealing/irradiation periods. Observation of bubbles at dislocations in austenitic alloys have been made after annealing of implanted material (100,119), after high temperature helium implantation (120) and after neutron irradiation (112,121,122). Helium bubbles were observed at Frank
dislocation loops and along dislocation line segments after helium ion implantation. Similarly, neutron irradiation of austenitic alloys results in the association of helium bubbles with both irradiation induced and deformation induced dislocations.

Ryazanov et al (123) recently studied the growth of helium bubbles at dislocations during annealing of helium implanted nickel. It was shown that gas bubbles at dislocations grow much more rapidly than in the bulk which was attributed to rapid diffusion of helium along the dislocations relative to substitutional helium diffusion in the matrix. Ganeyev (124) proposed a model whereby bubbles at dislocations may be ordered due to an elastic interaction which controls the bubble spacing along the dislocation. The optimum bubble spacing corresponded to an energy minimum and was only operative for bubbles at edge dislocations. Such an interaction would inhibit the coalescence of bubbles at dislocations.

Helium bubbles which do not nucleate on dislocations may be attracted to dislocations due to elastic interactions. The attractive interaction causes a long range drift of bubbles to dislocations and a high local binding of bubbles to the dislocation line (96). Weeks et al (125) differentiated between the long range and short range interactions in a theoretical analysis. The long range interaction energy of a bubble with straight screw and edge dislocations in isotropic solids was derived assuming bubbles to be spherical inclusions with zero bulk and shear moduli. For a bubble with radius \( r \), having a position \((R, \theta)\) about the dislocation line, the interaction energy with a screw dislocation, \( E_s \), is:

\[ E_s = \frac{3 \pi r^3 \mu}{8 \sqrt{2} (1 - \nu)} \]
The interaction energy with an edge dislocation, $E_e$, is:

$$E_e = -\frac{5Gb^2r^3}{2\pi R^2} \left[ \frac{1-(1+6\nu-5\nu^2\sin\theta)}{5} \right] \frac{1}{(7-5\nu)(1-\nu)}$$

Where $b$ is the Burgers vector, $\nu$ is Poissons ratio and $G$ is the shear modulus. Similar expressions for screw dislocations are given by Lin and Mura (126) and by Willis et al (127).

The expressions for the long range interaction are only valid for $R>5r$. When a bubble lies close to or at the dislocation core then a short range interaction must be considered. Barnes set the interaction energy equal to the energy of the removed dislocation line (128). The interaction energy of a bubble of radius $r$, with a dislocation is thus:

$$E = -rGb^2$$

Cahn estimated the interaction energy as the elastic energy originally stored in the volume occupied by the bubble (129) and Weeks et al extended this treatment to give (125):

$$E_s = \frac{Gb^2r^3}{2\pi} \left( \pi^2 + \ln\left(\frac{r}{R_o}\right) \right)$$

where $R_o$ is the core radius.

The long and short range interaction energies between a bubble and a dislocation result in an attractive force causing bubbles to drift towards dislocations and a pinning force essentially trapping a bubble at a dislocation. Weeks et al (125) derived an expression for the attractive force between a bubble and a screw dislocation, $F_s$:

$$F_s = \frac{5Gb^2r^3}{\pi} \frac{(1-\nu)}{(7-5\nu)} \frac{1}{R^3}$$
Similar relationships exist for edge dislocations where:

$$ F_e = \left( \frac{a}{h} \right)^3 $$

Weeks et al (125) derived a further expression defining the volume of radius $R^*$ from which all bubbles should be drawn onto a straight screw dislocation in time $t$ (assuming surface diffusion controlled bubble migration):

$$ R^* = \left[ \frac{16 D_s^2 G \Omega^2 (1-v)}{\pi^2 kT r (7-5v)} \right]^{1/4} $$

where $D_s$ is the surface diffusion coefficient and $\Omega$ the atomic volume.

Bubbles are effectively pinned to a dislocation and migration is limited to motion along the defect. Beere found rapid migration of bubbles along stationary dislocations in copper and interpreted the result in terms of enhanced formation of surface steps (130). When the dislocation line is stressed the bubbles produce a pinning force, $F_p$. Dislocation motion is constrained by migration of the bubble and the dislocation will bow out. The pinning force is given as (94,96):

$$ F_p = G b^2 \cos \theta $$

where $\theta$ is the half-angle between the two dislocation segments at their point of intersection with the bubble surface. Weeks et al (125) give the condition for bowing out before a dislocation is pulled from the bubble as:

$$ -E_m > gb^2 r \ln \left( \frac{a^*}{r_0} \right) $$

where $E_m$ is the short range interaction energy, $a^*$ the outer cut off radius (bubble radius) and $r_0$ is the inner cut off radius (core radius).
3.4.3 HELIUM BUBBLES AT PARTICLE-MATRIX INTERFACES

It has been known for many years that gas bubbles are pinned by second phase particles in nuclear fuels (131). Swelling is markedly reduced by a high density of very fine precipitates because many bubbles can be pinned. Stainless steels are particularly prone to precipitation during high temperature irradiation as well as during thermal ageing. Helium bubbles have been reported at precipitate-matrix interfaces where the precipitate may be MC-type (105,132), $M_{23}O_6$ (105), Laves phase (121,133), Eta phase (132) or G-phase (132). TiC is a particularly powerful trap for helium. Helium bubbles form at TiC/matrix interfaces in preference to other precipitate interfaces and even to grain boundaries (105).

The question why TiC particles exhibit strong trapping for helium remains largely unanswered. Maziasz (134) invokes an atomistic argument based on diffusion and segregation. TiC is a highly biased vacancy absorber during growth due to a 60-70% volume increase during precipitation. Maziasz argues that helium is supplied to the interface via the flux of vacancies and results in preferential bubble nucleation and growth. Kesternich and Rothaut (105) use an alternative argument to explain their results; they postulate that interfacial dislocations at the TiC/matrix interface act as strong traps for helium. It was suggested that a fine dislocation network (1nm spacing) exists due to the 17% lattice mismatch between the precipitate and the matrix the cores of which act as strong trapping sites for atomic helium.

Helium bubbles at particle-matrix interfaces are effectively
pinned because the bubble size and shape is modified to create a balance between the surface tension and interfacial tension and to minimise the total free energy of the system. The binding energy, $E_b$, was estimated by Nelson (135) assuming a flat, rigid precipitate and that the expansion of the bubble maintains a new equilibrium pressure:

$$E_b = -8\pi r^2 \gamma_s \log_2 \left[ \frac{4 - (1 - \cos \theta)^2 (2 + \cos \theta)}{4 \cos \theta} \right]^{-1/2}$$

where $r$ is the bubble radius, $\gamma_s$ is the surface tension of the matrix and $\theta$ is the contact angle.
CHAPTER FOUR. RADIATION DAMAGE TO METALS

4.1 INTRODUCTION

The subject of radiation damage to metals is too broad to be fully covered here. Discussion is limited to the formation and clustering of point defects as dislocation loops and voids. Particular emphasis is given to the role of grain boundaries as sinks for point defects. The simulation of radiation damage due to fusion neutrons is also considered.

4.2 THE DEVELOPMENT OF RADIATION INDUCED MICROSTRUCTURES

Radiation damage to metals results from the displacement of atoms by high energy particles, which may be electrons, neutrons, protons, heavy-ions or light-ions. If a lattice atom receives an energy, through collision, in excess of the displacement energy (typically 25eV) it can leave the lattice site and become displaced within the solid as an interstitial atom. A Frenkel defect is formed. The energy of the displaced atom is dependent on the energy and type of incident particle; for example, 1MeV electrons produce low energy recoil atoms and result in isolated displacements. In contrast, 2MeV neutrons produce recoil atoms with sufficient energy to cause further displacements. The result is a collision cascade where many displacements occur per incident particle. At the end of the trajectory of a recoil atom a large amount of energy is deposited in a small volume and the displaced atoms tend to migrate rapidly away by focussed collision sequences, leaving behind a high local concentration of vacancies. This displacement cluster can collapse to
a two dimensional vacancy loop (136). Many Frenkel defects recombine by rapid diffusion of interstitial atoms to vacancies but surviving interstitials can cluster to form dislocation loops.

Vacancy-type and interstitial-type dislocation loops have been reported in neutron irradiated stainless steels (see Table 4.1).

<table>
<thead>
<tr>
<th>TEMPERATURE (°C)</th>
<th>DISLOCATION MICROSTRUCTURE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;325</td>
<td>Vacancy loops and interstitial loops form.</td>
<td>141</td>
</tr>
<tr>
<td>325-500</td>
<td>Vacancy loops only stable up to 400°C. Interstitial Frank faulted loops predominant, some loops unfaul.</td>
<td>137, 141-143</td>
</tr>
<tr>
<td>500-600</td>
<td>The degree of unfaulnting increases.</td>
<td>12</td>
</tr>
<tr>
<td>600-700</td>
<td>Dislocation networks develop.</td>
<td>141, 143</td>
</tr>
<tr>
<td>&gt;700</td>
<td>Thermal vacancies dominate point defect interactions and Frank loops do not form.</td>
<td>12</td>
</tr>
</tbody>
</table>

Vacancy loops are only observed at irradiation temperatures below 673K (137, 138). At higher temperatures vacancy loops are annihilated by one of a variety of mechanisms (137):

1. Thermal emission of vacancies to alternative sinks.
2. Arrival of interstitial atoms.
3. Dislocation movement by glide and climb during irradiation may sweep up vacancy loops.
4. Large vacancy loops may unfaulnt and are then able to glide.

Interstitial dislocation loops are stable against thermal
emission due to the high formation energy associated with self-interstitial atoms. Consequently, interstitial loops are stable up to much higher temperatures (Table 4.1). The existence of interstitial dislocation loops in irradiated metals has been known for many years (139). Barnes (140) showed that the insertion of a monolayer platelet of atoms on a (111) plane produces an extrinsic stacking fault bounded by a dislocation with Burgers vector \( \mathbf{b} = \mathbf{a}/3(111) \). Such a sessile loop can dissociate by the passage of two Shockley partial dislocations (one above the extra plane and one below) to form a perfect prismatic dislocation:

\[
\frac{a}{3}[111] + \frac{a}{6}[\bar{1}2\bar{1}] + \frac{a}{6}[\bar{1}1\bar{2}] = \frac{a}{2}[011]
\]

The driving force for the reaction is the energy gained by removing the stacking fault.

Neutron irradiation results in the formation of Frank-faulted loops in austenitic steels (Table 4.1). At high irradiation temperatures the degree of unfaulting increases; dislocations then glide and climb to form dislocation networks. The temperature dependence of dislocation structure is similar during heavy-ion irradiation (Table 4.2).
The formation of dislocations in austenitic stainless steels during heavy-ion irradiation.

<table>
<thead>
<tr>
<th>TEMPERATURE (°C)</th>
<th>ION-IRRADIATION/ DISLOCATION STRUCTURE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>40-200keV chromium-ion irradiation produces both vacancy and interstitial loops.</td>
<td>144</td>
</tr>
<tr>
<td>525</td>
<td>20MeV carbon-ion irradiation produces Frank faulted loops at low doses. Unfaulting and climb produces networks at high doses.</td>
<td>145</td>
</tr>
<tr>
<td>400-600</td>
<td>46.5MeV nickel-ion irradiation produces Frank faulted loops, some unfault. The loop density decreased and loop radius increased with temperature.</td>
<td>146</td>
</tr>
</tbody>
</table>

Radiation induced voids are an additional important feature of the microstructure of neutron irradiated stainless steels. Cawthorne and Fulton presented the first experimental evidence for void formation (147); voids lead to dimensional and mechanical instability in fission reactor structural materials. Voids are also expected to contribute to swelling in first wall materials of future fusion reactors. Void swelling has been studied extensively (148) and theoretical treatments have successfully described the main features of the phenomenon (61,149). Voids are three dimensional clusters of irradiation induced vacancies and are formed in the temperature range $0.25T_m$ to $0.5T_m$. However, voids are distinguished from bubbles in that their existence depends on an excess of vacancies over the thermal equilibrium value; voids are unstable above $0.5T_m$ due to vacancy emission. Bubbles are filled with gas so are stable against vacancy emission at high temperatures.

The excess flux of vacancies to voids is due to the biased
absorption of interstitial atoms at dislocations. The larger elastic strain-field associated with self-interstitial atoms favours the loss of interstitials to dislocations leaving a net vacancy concentration. The development of voids therefore requires the presence of dislocations; these may be irradiation induced or due to cold work. Furthermore, there is growing evidence that gases are essential to void nucleation (61,150). Helium is a powerful promoter of cavity formation (150). The presence of gas stabilises a small void against collapse to a dislocation loop, which is the lowest energy configuration for small vacancy clusters. Small gas bubbles grow by the addition of gas atoms. However, there exists a critical radius above which the arrival rate of vacancies into a bubble exceeds the rate of thermal emission (151). This is due to the dislocation bias for interstitial atoms. Hayns gives the critical radius, \( r_c \), as:

\[
 r_c = \frac{2YDZ_IZ_V\Omega\rho}{(Z_I-Z_V)KkT}
\]

Where \( \gamma \) is the surface energy; \( D \) is the self-diffusion coefficient; \( Z_I \) and \( Z_V \) are the interstitial and vacancy dislocation bias factors; \( \rho \) is the dislocation density; \( \Omega \) the atomic volume; \( K \) the dose rate (dpa/s) and \( k \) and \( T \) are Boltzmann's constant and the absolute temperature. The critical cavity size model for void nucleation envisages helium in the form of small bubbles of which the larger ones exceed the critical size for bias driven growth.

Void swelling has received considerable theoretical treatment. In a simple analysis, where point defect recombination is considered negligible, the swelling rate i.e. the fractional change in volume, \( S \), with damage dose, \( \phi \) (dpa) can be expressed (152):
\[ \frac{dS}{d\phi} = 4\pi r_v C_v (Z_v - Z) \rho \]

\[ \frac{dS}{d\phi} = \frac{(A-1)}{(y+A/y+A+1)} \]

Where A is the dislocation bias term (if \( Z_v = 1 \) then \( Z = A \)).

**4.3 GRAIN BOUNDARIES AS SINKS FOR POINT DEFECTS DURING IRRADIATION**

Grain boundaries are known to act as sinks for point defects (154) and can play a major role in absorbing radiation induced vacancies and interstitials (155). Balluffi recently reviewed models and experimental evidence for the point defect sink behaviour of high angle grain boundaries (154). The operation of a grain boundary as a sink is generally a complex process involving a number of steps which include diffusion of point defects to the boundary, diffusion of defects in the boundary and ultimate annihilation either at jogs on secondary grain boundary dislocations (SGBDs) or by recombination with an opposite defect. Exact coincidence boundaries do not contain SGBDs and to act as point defect sinks it is necessary to nucleate SGBD loops.

Balluffi suggests that point defects migrate in a boundary whilst retaining a basic identity as a missing or extra atom (154). However, a vacancy may become dissociated at an interface and diffuse more rapidly than a lattice vacancy. There is little data available for the diffusion rate of self-interstitial atoms at grain boundaries.
Balluffi argues that the interstitial diffusion rate may be slower than in the lattice because there are sites of high binding energy in the interface. In contrast, interstitials are essentially unstable in the lattice and diffuse easily.

Experimental observation of point defect loss at boundaries consists of direct observation in the electron microscope (156,157) or indirectly from the presence of zones denuded of point defect clusters. Komem et al. (156) directly observed the climb of extrinsic SGBDs in twist boundaries in gold exposed to ion irradiation. King and Smith (157) similarly observed the climb of intrinsic SGBDs in off-coincidence boundaries during electron irradiation. Furthermore, King and Smith identified the coherent twin as a sink for self-interstitials by a mechanism of dislocation loop nucleation and growth in the interface (157). Indirect evidence for the point defect sink behaviour of grain boundaries came originally from quenching experiments (e.g.158). The presence of zones denuded of vacancy clusters adjacent to grain boundaries was explained by a reduction in the vacancy concentration adjacent to grain boundaries below that necessary for cluster nucleation (158). Quenching experiments showed that the size of the denuded zone is, in general, insensitive to boundary misorientation although the coherent twin interface may exhibit some or no denudation depending on the vacancy supersaturation (154).

Irradiation induced vacancies and interstitials can cluster to form dislocation loops and voids. Zones denuded of these clusters can develop in the vicinity of grain boundaries. Interstitial loss at grain boundaries results in a dislocation loop denuded zone as
reported in neutron irradiated copper (159), proton irradiated aluminium (160) and neutron irradiated aluminium (161). In marked contrast, Farrell reports enhanced nucleation of dislocation loops in the immediate vicinity of grain boundaries in a neutron irradiated aluminium alloy, but no explanation was forwarded (162). Void denudation has received considerable attention due to the possibility of suppressing void swelling in fine grained materials (155); void denuded zones have been reported in a number of irradiated materials (Table 4.3). Denuded zones are generally symmetrical about the boundary and are typically 0.1-0.2\mu m wide, the width being dependent on irradiation temperature (161,166). Vacancy mobility is enhanced at higher temperatures so the region depleted of vacancies at grain boundaries is larger (168).

Some anomalous behaviour associated with void denudation has been reported. Non-symmetrical denuded zones have been observed in a variety of irradiated metals, which include nickel (163,164,166), and stainless steel (167). The observation is generally attributed to boundary migration during irradiation. Vaidya recently demonstrated void-assisted grain boundary migration in an ion-irradiated austenitic stainless steel (169).
### Table 4.3: Observations of void denuded zones at grain boundaries.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TYPE OF IRRADIATION</th>
<th>TEMPERATURE (°C)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>neutron</td>
<td>327</td>
<td>159</td>
</tr>
<tr>
<td>Nickel</td>
<td>4MeV nickel-ions</td>
<td>594</td>
<td>163</td>
</tr>
<tr>
<td>Nickel</td>
<td>20MeV carbon-ions</td>
<td>525</td>
<td>164</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.8MeV nickel-ions</td>
<td>625</td>
<td>165</td>
</tr>
<tr>
<td>Nickel</td>
<td>neutron</td>
<td>260</td>
<td>166</td>
</tr>
<tr>
<td>Nickel</td>
<td>neutron</td>
<td>380</td>
<td>166</td>
</tr>
<tr>
<td>Nickel</td>
<td>neutron</td>
<td>500</td>
<td>166</td>
</tr>
<tr>
<td>Nickel</td>
<td>neutron</td>
<td>575</td>
<td>166</td>
</tr>
<tr>
<td>Fe-20Ni-20Cr</td>
<td>1MeV electrons</td>
<td>600</td>
<td>155</td>
</tr>
<tr>
<td>Fe-17Cr-17Ni +2.5Mo</td>
<td>Triple-ion</td>
<td>827</td>
<td>167</td>
</tr>
<tr>
<td>Aluminium</td>
<td>neutron</td>
<td>55</td>
<td>161</td>
</tr>
<tr>
<td>Aluminium</td>
<td>neutron</td>
<td>150</td>
<td>161</td>
</tr>
<tr>
<td>Aluminium</td>
<td>neutron</td>
<td>55</td>
<td>168</td>
</tr>
</tbody>
</table>

* Estimated from published micrograph.

Anomalously large voids can grow at the edge of denuded zones. The effect has been reported in neutron irradiated copper (159) and aluminium (168) and in ion-irradiated nickel (163,164). Farrell suggests that the effect is due to the difference in mobility between interstitials and vacancies (168); interstitials are highly mobile and are depleted from a wider band than the equivalent band for vacancies. A region of excess vacancies results where the interstitial concentration but not the vacancy concentration is reduced. The local vacancy concentration enhances rapid void growth. An alternative explanation, due to Norris (170), involves a local, non-uniform distribution of dislocations providing a local sink for excess interstitials, thereby allowing a high vacancy flux to growing
voids. Chen and Buttry report large voids within the denuded zone (163) and account for the observation by the nucleation of gas bubbles (void nuclei) in the denuded zone at some pre-existing heterogeneity or by the release of gas bubbles into the denuded zone. The isolated bubbles act as void nuclei and since these are the only vacancy sinks within the denuded zones they grow to large sizes (163).

In contrast to void denudation at grain boundaries, Norris (171) reported enhanced void nucleation and growth at coherent twin interfaces in electron irradiated nickel. In contrast, Chen and Buttry (176) reported void denudation at both coherent and incoherent twin interfaces in ion irradiated nickel; the denuded zones were much smaller at the coherent interfaces. Norris argued that enhanced void nucleation and growth in the vicinity of coherent twin interfaces results from the preferential loss of interstitial atoms at the interface (171). King and Smith (157) recently reported interstitial loss at coherent twin boundaries by the nucleation and growth of interstitial dislocation loops at the interface. The conflicting evidence of Chen and Buttry for inhibited void growth at coherent twin interfaces cannot be accounted for using this argument. It may be that the sink efficiency for interstitial atoms is dependent on the interstitial supersaturation in a similar way to that proposed by Balluffi for vacancy loss at coherent twins (154).

4.4 SIMULATION OF FUSION NEUTRON RADIATION DAMAGE

First wall materials in fusion reactors will be subject to a severe irradiation environment. High fluxes of 14MeV neutrons will produce displacement damage and induce nuclear transmutation reactions
which generate high levels of helium and hydrogen. To aid our understanding of materials response to this environment and in the absence of a working fusion reactor, it has been necessary to simulate fusion neutron irradiation. A variety of experimental techniques have evolved which simulate the anticipated fusion neutron damage (121). These include the use of dual- or triple-ion beam equipment, fast spectrum or mixed spectrum fission neutrons and low flux, high energy neutron sources.

Spitznagel et al (121) have reviewed the techniques available for simulating the damage due to fusion neutrons. Mixed spectrum fission reactors provide a wide range of neutron energies and irradiation can produce both atomic displacement damage and controllable amounts of helium in alloys containing nickel. The helium is produced by thermal neutrons via the two step reaction:

\[ {\text{^{58}Ni} + n} \rightarrow {\text{^{59}Ni} + \gamma} \]
\[ {\text{^{59}Ni} + n} \rightarrow {\text{^{56}Ni} + ^{4}\text{He}} \]

The technique is particularly useful for austenitic alloys since they contain nickel as a major constituent. High energy neutron sources can produce low fluxes of neutrons with energies in the range 1-30MeV and can be used to study cascade structure, defect survivability and the early stages of point defect clustering (172).

4.4.1 ION BEAM SIMULATION OF NEUTRON IRRADIATION DAMAGE

Ion accelerators offer an alternative technique for the simulation of fusion neutron irradiation. Neutron damage simulations have, in the past, consisted of heavy-ion irradiation of helium pre-implanted material. Pre-implantation can give misleading results
due to an unrepresentative supersaturation of helium; the problem is worse for fusion simulations where high levels of helium are involved. The dual-beam technique was developed to solve the pre-implantation problem. The continuous production of helium during neutron irradiation is simulated by implanting helium ions together with heavy ions at high temperatures. The major advantages of the dual-beam technique over other simulation methods are that it is not specific to nickel bearing alloys and can be applied to the refractory alloys, an important group of candidate materials for first wall applications. Furthermore, the ratio of the helium injection rate to the rate of displacement damage (appmHe/dpa) is easily varied.

The advantages of using ion-beam techniques for the simulation of neutron radiation damage can be summarised (150,152):

1. High damage levels in short times.
2. Reveals details of microstructural development.
4. No residual radioactivity.
5. Independent control of irradiation variables.
7. Control of helium concentration.

The disadvantages can be summarised (150,152):

1. Dose rate effects; to compare swelling due to neutron irradiation the rapid simulations require a temperature compensation of as much as +200K.
2. Transmutation products are not generated in single-beam experiments.
3. The damaging ion is an extra interstitial or foreign atom and can
participate in the evolution of damage structure (Table 4.4).

4. The damaged region is generally within 1µm of a free surface which can modify the damage structure by;
   a. acting as a sink for point defects,
   b. loss of dislocations by glide,
   c. interference of atmospheric impurities.

5. Small samples offer limited irradiated volume generally only suitable for TEM.

6. The displacement event is different to neutron irradiation and results in a problem of dose equivalency.

The disadvantages of self-ion injection (reduced swelling rate) and of point defect loss to surfaces (void and loop denudation) can be significant (Table 4.4), particularly for low energy ion irradiation (<1MeV) where both displacement damage and ion-injection occur near to a free surface. An additional consideration when using ion beam simulation is the problem of dose equivalency. During fast neutron irradiation a large proportion (99%) of the point defects produced are due to primary recoil atoms (180), the displacement cascades are large. For 46.5MeV nickel-ion irradiation about 80% of the displacements are due to recoil atoms; for 20MeV carbon-ions this reduces to about 50% and for 5MeV protons only 40% of displacements are due to recoil atoms (194). The displacement cascades produced by ion-irradiation are smaller than those due to neutron irradiation. Nelson et al (181) argue that small displacement cascades allow less in-cascade recombination and a large fraction of radiation induced point defects survive. The argument was based on the observation of low swelling rates in nickel and austenitic stainless steel during 46.5MeV nickel-ion irradiation compared to that observed during 20MeV
carbon-ion irradiation (181). Clearly, ion-irradiation cannot be used as a direct simulation for neutron damage.

<table>
<thead>
<tr>
<th>PROBLEM</th>
<th>EVIDENCE</th>
<th>OBSERVATIONS/COMMENTS</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-ion injection</td>
<td>Theoretical (rate- theory)</td>
<td>Large reduction in void swelling especially if point defect recombination or unbiased sinks dominate point defect loss.</td>
<td>173</td>
</tr>
<tr>
<td>Self-ion injection</td>
<td>Theoretical (rate- theory)</td>
<td>The void-swelling rate can be significantly reduced, particularly at low dislocation densities.</td>
<td>153</td>
</tr>
<tr>
<td>Self-ion injection</td>
<td>Experimental</td>
<td>Significant reductions in swelling during 4MeV nickel-ion irradiation of 316 stainless steel were reported.</td>
<td>174</td>
</tr>
<tr>
<td>Free surfaces</td>
<td>Theoretical (rate- theory)</td>
<td>Significant point defect loss to surfaces at high temperatures and low dislocation densities.</td>
<td>175</td>
</tr>
<tr>
<td>Free surfaces</td>
<td>Theoretical (rate- theory)</td>
<td>Minimal surface losses for 46.5MeV nickel-ion irradiation of stainless steel but significant point defect losses with 4MeV nickel-ions.</td>
<td>176</td>
</tr>
<tr>
<td>Free surfaces</td>
<td>Theoretical (rate- theory)</td>
<td>Point defect loss predicted to produce a 75mm wide zone denuded of dislocation loops.</td>
<td>177</td>
</tr>
<tr>
<td>Free surfaces</td>
<td>Experimental</td>
<td>30nm wide void-free zone at the surface of 100keV nickel-ion irradiated nickel.</td>
<td>178</td>
</tr>
<tr>
<td>Free surfaces</td>
<td>Experimental</td>
<td>50nm wide void-free zone at the surface of a variety of austenitic alloys after 5MeV nickel-ion irradiation.</td>
<td>179</td>
</tr>
</tbody>
</table>

Dual-beam experiments have been used to study the microstructural effects of simultaneous helium implantation and displacement damage. The technique cannot directly simulate neutron effects due to the disadvantages outlined above but can be used to study critical
parameters such as the helium/dpa ratio, temperature and dose rate. Results from dual-beam experiments have been reviewed (121,182). The majority of experiments to date have addressed the problem of swelling with helium/dpa ratios typical of fusion conditions (20 appm He/dpa) and the results can be summarised (182):

1. Increasing the He/dpa ratio causes higher densities of cavities and loops. Bimodal cavity size distributions are frequently observed, consistent with a model for the bias-driven growth of voids nucleated on critically sized bubbles.

2. Varying degrees of loop enhancement with helium implantation have been reported. The total dislocation density is relatively insensitive to the He/dpa ratio.

3. The effect of increasing the He/dpa ratio on swelling is complex and may either increase or decrease the overall swelling. In general, small amounts of helium promote cavity nucleation and increase cavity volume fractions, particularly in swelling resistant alloys. Larger amounts of helium may increase cavity and loop densities to the point where swelling is retarded.

4. Swelling during dual-beam irradiation is temperature dependent. The swelling peak is shifted to higher temperatures relative to neutron irradiation. Increases in the He/dpa ratio may increase swelling at high temperatures and either increase or decrease swelling at temperatures below the peak swelling temperature.

The development of cavities at grain boundaries during dual-beam irradiation has received limited attention, despite the known problem of helium embrittlement. Farrell and Packan (167) observed cavities at grain boundaries in a model austenitic alloy (Fe, 17%Cr, 16.7%Ni,
2.5%Mo) after triple-beam irradiation at 900-1100K. Nickel-, helium-(20He/dpa), and deuterium-ions (50D/dpa) were used to simulate the simultaneous generation of helium and hydrogen during fusion neutron irradiation. Packan (183) also reports grain boundary cavities after dual-beam irradiation of the same material. Pulsed irradiation resulted in slightly fewer but larger cavities at grain boundaries. Grain boundary cavities are generally taken to be gas-filled because voids are unstable at grain boundaries (167). Farrell and Packan (114) measured the size and density of grain boundary cavities in Nimonic PE-16 alloy which was triple-beam irradiated at 898K. A high density of bubbles was reported at grain boundaries but anomalously large cavities were identified at incoherent twin interfaces (Table 4.5). The size of bubbles at grain boundaries increased with dose but bubble density remained approximately constant.

<table>
<thead>
<tr>
<th>IRRADIATION CONDITIONS (ALL AT 898K)</th>
<th>INCOHERENT TWIN BUBBLE SIZE</th>
<th>INCOHERENT TWIN BUBBLE DENSITY</th>
<th>GRAIN BOUNDARIES BUBBLE SIZE</th>
<th>GRAIN BOUNDARIES BUBBLE DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>dpa appmHe appmD*</td>
<td>(nm)</td>
<td>(x10^13 m^-2)</td>
<td>(nm)</td>
<td>(x10^15 m^-2)</td>
</tr>
<tr>
<td>80 11 28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180 8.5 21</td>
<td>60-93</td>
<td>4.0</td>
<td>6.0</td>
<td>1.2</td>
</tr>
<tr>
<td>313 10 25</td>
<td>98</td>
<td>2.0</td>
<td>5.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

* D=deuterium
4.5 SUMMARY

Helium will be generated by transmutation reactions in the first wall of a fusion reactor; high energy neutrons will also create displacement damage inducing both dislocations and voids. To understand the role of helium in the development of these irradiation induced microstructures (and in the absence of a high energy, high flux neutron source) it is necessary to simulate the expected irradiation conditions. Dual-ion beams have been used to simulate the simultaneous generation of helium and displacement damage; the majority of experiments to date have been used to study the role of high helium generation rates on void swelling. Despite the problem of helium embrittlement no systematic work has been reported describing the nucleation and growth of helium bubbles at grain boundaries under simulated fusion conditions.
CHAPTER FIVE. EXPERIMENTAL METHOD

5.1 INTRODUCTION

The major aim of this work is to characterise the role of grain boundaries as preferential sites for the nucleation and growth of helium gas bubbles. A single phase austenitic alloy was used as a model for 316 stainless steel. The dual-beam facility at AERE Harwell was used to irradiate the austenitic alloy. The nucleation and growth of helium bubbles was studied during helium-ion and dual-beam irradiation at elevated temperatures. Irradiation induced microstructures were subsequently studied using transmission electron microscopy (TEM). Particular emphasis was given to the roles of grain boundary structure, temperature, gas implantation rate and dual-beam irradiation upon the nucleation density of bubbles at grain boundaries. Consideration was also given to microstructural development within grains and to the nucleation and growth of dislocation loops at coherent twin interfaces and adjacent to some grain boundaries.

5.2 MATERIAL

The nominal composition of the ternary austenitic alloy was Fe,15%Cr,15%Ni with estimated impurities as shown in Table 5.1. For comparison, the specification for commercial 316 stainless steel is also given. The ternary alloy was cast using iron (0.006%C), chromium (<50appmC) and nickel (<0.001% metallic impurities) as starting materials (184) and was supplied as cold-worked strip (0.56mm thick). The strip was subsequently annealed at 1050°C for 30 minutes and
cold rolled in stages to a thickness of 0.2mm. 3mm discs, suitable for TEM were punched from the strip prior to a final anneal under vacuum at 750°C for 30 minutes. The total thickness reduction during cold rolling was 65% and the low temperature annealing treatment resulted in a fine grain size of 6µm (determined optically). Use of a fine grain size ensured that each TEM specimen contained numerous grain boundaries for analysis.

<table>
<thead>
<tr>
<th>TABLE 5.1</th>
<th>Composition of the ternary austenitic alloy and of commercial 316 stainless steel.</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFERENCE</td>
<td>ALLOY</td>
</tr>
<tr>
<td>184</td>
<td>Ternary alloy</td>
</tr>
<tr>
<td>185</td>
<td>316 stainless steel</td>
</tr>
</tbody>
</table>

5.3 ELECTROPOLISHING

Use of the dual-beam facility involves implanting helium within a depth of 0.2µm below the irradiated surface. Two techniques were used to prepare irradiated thin film specimens. Pre-thinned electron transparent discs were irradiated to determine the experimental variables appropriate to the use of the dual-beam facility. However, due to uncertainty about foil temperature during irradiation (section 5.4.1) and about point defect loss to surfaces most disc specimens were irradiated prior to thinning (Figure 5.1). First, a pre-irradiation polish was used to remove surface oxide and produce a clean face for ion-irradiation. A dished profile was formed on the polished face to ensure a suitable profile for subsequent thinning (Figure 5.1). Specimen preparation was developed to retain the implanted layer within the electron transparent region of the thin
film. The irradiated face of the disc was protected during electropolishing by Lacomit (an acetone-based varnish). The back of each disc was removed by electropolishing to produce perforated foils suitable for TEM (Figure 5.1).

Each electropolishing stage involved using a 5% solution of perchloric acid in methanol in a Struers-Tenupol jet polishing unit. To ensure controlled polishing rates and for safety reasons the solution was cooled to <-50°C. Electropolishing was carried out at a voltage of 60V and 15mA of current. The jet polishing unit, operated by an automatic cut-off, ensured a high degree of success (better than 70%) in producing thin films suitable for TEM.

5.4 THE DUAL-BEAM FACILITY

The dual-beam facility at AERE Harwell consists of two ion-accelerators aligned along beam lines which converge onto a single target chamber. The facility was used for simultaneous irradiation with helium- and chromium-ions and also for single beam irradiation (He⁺ or Cr⁺) using one accelerator alone. A schematic plan of the dual-beam facility is shown in figure 5.2. The Cockroft-Walton 500KeV accelerator and the 80KeV accelerator both consist of an ion-source and a mass-analysing magnet which are aligned onto the target chamber. Each beam line has an independent vacuum system which maintains a vacuum better than 10⁻⁶ mbar. A vacuum of <5x10⁻⁶ mbar is maintained in the target chamber during irradiation. Quadrupole lenses on each beam line act as beam condensers and electrostatic X-Y scanners are included for optional beam scanning. The beam lines converge at an angle of 55° at the
The target stage (Figure 5.3) is housed in the target chamber and is mounted rigidly on a stainless steel base plate which, when fitted to the chamber, ensures that the target is positioned correctly relative to both ion beams. A large ceramic-metal seal is welded into the centre of the base plate and has the heater support pillar brazed into it. The total beam current striking the target can be monitored through this seal. Six additional ceramic-metal seals provide electrical leads into the vacuum chamber, two are used as heater terminals, one as a lead through for the chromel-alumel thermocouple, one provides contact to the suppression-bias plate and two leads allow constant monitoring of the beam on the two probe assemblies.

During single beam irradiations, the beam current is measured using a Hewlett-Packard multi-meter which measures the current flow to earth from the target stem. Secondary electron emission from the target due to the incident ion beam is suppressed by the application of a negative (-250V) potential to the suppression bias-plate. The suppression bias-plate is a circular, stainless steel plate with a segment removed. Welded to the bias plate is a Faraday cup with part of one side cut away to allow the helium ion beam to strike the target. The biased Faraday cup acts to suppress both secondary electron emission from the target and thermionic electrons from the heater.

The problem of monitoring two incident ion beams during dual-beam operation was overcome by a modification to the collimator assembly. The original target stage (186) did not include the two
probe-assemblies shown in figure 5.3. The stainless steel earthed bias-plate incorporated two detachable collimators which were independently aligned to ensure that the two collimated beams struck the target. However, only the total beam current striking the target could be measured. To overcome this problem, two annular probes in the form of adjustable collimators were included. These are electrically insulated from the rest of the target stage and sample the outer annulus of the collimated beams. Suppression of the probes was not possible due to the limited space within the target chamber so true beam current was not measured. Instead, the monitored current on the annular probe was calibrated with true (suppressed) target current for each ion beam prior to irradiation. In this way, it was possible to monitor each ion beam independently and to measure the total suppressed current striking the target.

The 3mm disc specimens were irradiated individually. Each specimen was mounted on top of the heater block (Figure 5.3) and was secured by a molybdenum cover plate. The heater consists of a non-inductively wound element on a molybdenum heater former and is enclosed in a stainless steel heat shield. A chromel-alumel thermocouple is located in a hole drilled horizontally in the top of the heater former 5mm below the specimen position. A Solartron stabilized DC source was used to power the heater. Temperature calibration of the heater was made using a constant voltage (20V) (Figure 5.4) and the temperature control during irradiation was +/-2°C at 600°C. Operation of the heater allowed heating and cooling under vacuum and typical heating and cooling rates are shown in Figure 5.5.
5.4.1. BEAM HEATING EFFECTS

The temperature of the heater block was monitored throughout irradiation. However, the possibility of beam heating exists whereby the temperature of the target is raised due to the energy deposited by the ion beam. In the case of bulk discs, where the back surface of the disc maintains thermal contact with the heater block, the heat is conducted away through the specimen and into the heater block which acts as an effective heat sink; the temperature rise at the target surface due to the incident ion beam is then <1°C. Irradiation of pre-thinned foils results in a significant temperature rise because the deposited energy cannot be conducted away; in this case, the temperature rise is controlled by radiation losses (187). The temperature rise due to an incident ion beam can be estimated using Stefan's Law (187):

\[ E = \varepsilon \sigma (T^4 - T_s^4) \]

Where \( E \) is the power (Wm\(^{-2}\)) radiated from the surfaces of a thin foil; \( \sigma \) is Stefan's constant (\( \sigma = 5.67 \times 10^{-8} \text{Wm}^{-2}\text{K}^{-4} \)), \( \varepsilon \) is the emissivity of the foil, \( T \) is the absolute temperature of the surroundings and \( T_s \) is the absolute temperature of the radiating surface. Under steady-state conditions the rate of heat loss by radiation equals the rate of heat input from the ion beam. During 380keV chromium-ion irradiation the current density is typically 2.5x10\(^{-3}\)Am\(^{-2}\). The emissivity of stainless steel is 0.3 (188); the temperature rise of a thin foil which loses heat by radiation from its surfaces is calculated as 10°C at an implantation temperature of 600°C. At lower temperatures, where heat losses due to irradiation are lower, the temperature rise due to beam heating is even higher (18° at 450°C).
Due to the uncertainty of the temperature during irradiation the majority of irradiations were made using bulk discs, where heat loss from the specimen is aided by conduction into the heater block. Bulk discs have the further advantage that only one free surface is adjacent to the irradiated region.

5.5 IMPLANTATION DOSE AND DISPLACEMENT DOSE CALCULATIONS

During ion bombardment of a solid the energetic ions lose their energy by collisions, some of which create atomic displacements; the ions eventually come to rest in the solid, close to the surface. The atomic displacement rate and the concentration of implanted ions both vary with depth into the target. The Harwell version of the E-DEP-1 computer code (189) was used to calculate the displacement dose (displacements per atom) and the implanted ion concentration as a function of depth for helium-ions and chromium-ions in the ternary austenitic alloy. The helium-ion beams used were incident at an angle of 55° to the target normal and the calculated damage and range curves were used to estimate the displacement dose (dpa) and implanted ion concentration resolved along a direction normal to the specimen surface. The displacement rate at any depth, x, normal to the surface is that produced at a distance y along the beam path (Figure 5.6 after(189)) where:

\[ x = y \cos \theta \]

Similarly, the range distribution can be resolved along a direction normal to the target surface. The peak of the range distribution is shifted nearer to the surface of the target and the peak height increases (for a given dose) since the implanted ions are concentrated in a thinner surface region. Figures 5.7 and 5.8a show the resolved
range and displacement peaks for 70keV and 40keV helium-ion irradiation. The dual-beam facility is limited to irradiation with mono-energetic ion beams; this limitation means that both displacement rates and ion-implantation rates are a function of depth. For simplification, in the following analysis the implanted helium concentration has been averaged over the depth of the resolved range curve and the mean displacement is approximated to half the peak displacement rate (as shown in figures 5.7 and 5.8).

Dual-beam irradiations were performed using chromium-ions (which are effectively self-ions of the target alloy) and helium-ions. Appropriate ion energies were chosen to match the helium-ion range peak with the displacement peak of the chromium-ion; the matched energies used were 40keV helium-ions and 380keV chromium-ions (Figure 5.8). The resolved helium range peak is shown $R_{He}=75\text{nm}$. The displacement dose due to $10^{19}\text{Cr ions m}^{-2}$ is 2dpa(+/-0.5dpa) over the depth of the helium implanted region.

Specimens were irradiated using constant beam currents and the ion dose ($\phi_i$) was calculated from:

$$\phi_i = \frac{I_i t}{A e}$$

Where $I_t$ is the beam current measured on the target, $t$ is the irradiation time, $A$ the area of the incident ion beam and $e$ the electronic charge. The area of the chromium-ion beam is the area of the final collimator ($1.96\times10^{-5}\text{m}^2$) whereas the area of the helium-ion beam is the resolved area of the final beam collimator ($3.42\times10^{-5}\text{m}^2$) since the beam is incident at an angle to the target normal. The displacement doses and implanted helium
concentrations were calculated from figures 5.7 and 5.8 using the approximations outlined above. The averaged displacement rates and implantation rates are shown in table 5.2 for measured beam currents of 1\(\mu\)A. Irradiations were made using beam currents in the range 0.01-0.5\(\mu\)A and the implanted ion concentration and displacement dose were calculated from Table 5.2. Some limitations of the Harwell Dual Beam Facility are outlined in the Appendix.

### TABLE 5.2
Displacement rate and helium implantation rate as a function of ion-beam current.

<table>
<thead>
<tr>
<th>ION-BEAM CURRENT</th>
<th>DOSE RATE</th>
<th>AVERAGE DISPLACEMENT RATE</th>
<th>AVERAGE HELIUM IMPLANTATION RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>helium 70keV</td>
<td>1.0 1.8x10^{17}</td>
<td>7.1x10^{-4}</td>
<td>10</td>
</tr>
<tr>
<td>helium 40keV</td>
<td>1.0 1.8x10^{17}</td>
<td>8.2x10^{-4}</td>
<td>13</td>
</tr>
<tr>
<td>chromium 380keV</td>
<td>1.0 3.2x10^{18}</td>
<td>6.4x10^{-2}</td>
<td>-</td>
</tr>
</tbody>
</table>

5.6 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy was used to study the irradiation induced microstructures. This section outlines the conditions used to image bubbles, dislocations and grain boundaries. The method of Kikuchi pattern analysis for the determination of grain boundary misorientation is briefly discussed. An analysis for the determination of the dislocation content of high angle and low angle grain boundaries is also given. The quantitative determination of bubble density within grains and at grain boundaries is also described.
5.6.1 BUBBLE IMAGES IN THE TEM

The contrast due to bubbles in electron microscope images is sensitive to diffraction conditions, foil thickness, bubble size and position in the foil. Theoretical calculations have shown that for bright-field images (190,191):

1. Bubbles exhibit strongest contrast in thin regions of the foil ($<\frac{3\sigma}{5\sigma}$)

2. Three effects contribute to contrast in two beam 'focus' conditions:
   a. normal absorption, because there is less material to scatter electrons in columns containing bubbles.
   b. foil thickness, the fluctuating nature of intensity through a foil results in bright or dark contrast of bubbles dependent on position in the foil.
   c. phase shift, when $s$ (the deviation parameter) ≠ 0, contrast can result from a phase shift in the diffracted wave. The phase shift is sensitive to both the deviation parameter and the bubble size and contrast may be above, below or equal to background intensity.

3. Ruhle and Wilkens (191) calculated the contrast due to 'out of focus' imaging of gas bubbles under two beam and many beam (systematic row) conditions. In an under-focus condition the bubble image is bright relative to background and is surrounded by alternate dark and bright Fresnel fringes; the fringe intensity is rapidly damped after the first. Conversely, over-focus imaging reverses the contrast.

In this work, optimum contrast was achieved using under-focus kinematical conditions. The size and density of bubbles was determined by an analysis of the bubble images. For spherical bubbles
the true bubble diameter is that contained inside the first dark Fresnel fringe (191). The density of bubbles within grains and at grain boundaries was measured for a variety of irradiation conditions. The major assumption made in this analysis was that all the bubbles nucleate within a depth equivalent to the total depth of the helium-range peak. Micrographs of bubbles were recorded from thicker regions of irradiated foils to ensure that the range peak was contained within the sampled volume of foil. The thickness of the region containing bubbles was assumed to be 150nm for 40keV helium-ion irradiation and 200nm for 70KeV helium-ion irradiation (Figures 5.7 and 5.8). The density of bubbles within grains, \( \rho_b \), is given simply by:

\[
\rho_b = \frac{N}{At}
\]

Where \( N \) is the number of bubbles counted within a sampled area \( A \) of thickness \( t \).

Similarly, the areal density of bubbles at grain boundaries was estimated using the same approximation for foil thickness. The bubble density at grain boundaries was measured from micrographs where there was no specimen tilt. This ensured simple geometry where the areal bubble density \( \rho_a \) was given by (see figure 5.9):

\[
\rho_a = \frac{N}{l(p^2 + t^2)^{1/2}}
\]

Where \( N \) is the number of bubbles counted in a length of interface \( l \), \( p \) is the projected boundary width and \( t \) the estimated foil thickness.

5.6.2 DISLOCATION ANALYSIS

Dislocations show strong contrast in the electron microscope under strong diffraction (dynamical) conditions. The determination of
the Burgers vector and interstitial/vacancy nature of dislocation loops is well established (192). Here, a Burgers vector analysis was made for both irradiation induced dislocation loops and secondary grain boundary dislocations (SGBDs); a brief summary of the technique is given here. Theoretical treatment of the contrast from dislocations shows that a screw dislocation is invisible when \( g \cdot b = 0 \), where \( g \) is the operating diffraction vector and \( b \) is the Burgers vector of the dislocation. For an edge dislocation the invisibility criterion becomes \( g \cdot b = 0 \) and \( g \cdot b \cdot u = 0 \), where \( u \) is the direction of the dislocation line. The determination of \( b \) is achieved by imaging the dislocations under two beam conditions with successively different diffraction vectors. When two (or more) diffraction vectors \( g_1 \) and \( g_2 \) are found for which the dislocation is invisible, the direction of \( b \) is given by \( g_1 \times g_2 \) since \( g_1 \cdot b = g_2 \cdot b = 0 \).

Alternatively, if a range of likely Burgers vectors are known then the direction of \( b \) may be determined by inspection of possible invisibility criteria. For lattice dislocations, the magnitude of \( b \) is generally assumed to be the smallest lattice vector in the determined direction. In FCC metals, the analysis of irradiation induced dislocations usually reduces to the differentiation between Frank faulted loops with \( b = a/3\langle111\rangle \) and perfect dislocation loops with \( b = a/2\langle011\rangle \).

The Burgers vectors of SGBDs are a consequence of the grain boundary structure (controlled by misorientation) and possible vectors are predicted by the DSC (displacement-shift-complete) theory of grain boundaries (193). The changes in the SGBD image with diffraction vector can be used to show consistency with possible SGBD configurations but unambiguous determination of the Burgers vector is
often complicated by the possible high index (small magnitude) vectors. The analysis of the Burgers vectors of SGBDs requires the use of two-beam conditions. Since a grain boundary separates two adjacent crystals it is possible to achieve strong diffraction conditions in either or both crystals. Simultaneous two-beam diffraction is achieved by orienting the specimen for two-beam diffraction in both grains. Furthermore, when both crystals contain planes with identical orientation and spacing it is possible to achieve a common diffraction vector where the direction and magnitude of the diffraction vector are identical in each crystal.

Irradiation may result in vacancy type or interstitial type dislocation loops within grains (section 4.2) and determination of loop type is simple if the loop nature of the dislocation is readily resolved. Having deduced the Burgers vector of a dislocation loop, the interstitial/vacancy nature can be determined by a method described by Mazey et al (192). The Burgers vector of a dislocation is defined by the FS/RH rule; if the positive direction around the loop is taken as clockwise, then the positive component of the Burgers vector normal to the loop is in a downwards sense for a vacancy loop and upwards for an interstitial loop, relative to the plane of the foil.

The image contrast from a loop will change from outside the true position of the dislocation to inside when the sign of \( g \cdot b \) changes. When adopting the FS/RH convention the loop will appear large (outside contrast) when \( g \cdot b > 0 \), and small (inside contrast) when \( g \cdot b < 0 \). The sign of \( b \) is determined by noting the change from inside to outside contrast with change in sign of \( g \). The inclination of the habit plane
of the loop must be determined since from the FS/RH rule:

\[ \mathbf{n} \cdot \mathbf{b} < 0 \quad \text{vacancy loops} \]
\[ \mathbf{n} \cdot \mathbf{b} > 0 \quad \text{interstitial loops} \]

Where \( \mathbf{n} \) is the upward drawn normal to the habit plane. The habit plane can be determined by a high angle tilt of the specimen in the microscope.

5.6.3 DETERMINATION OF GRAIN BOUNDARY CRYSTALLOGRAPHY

Transmission electron microscopy showed that grain boundary structure is an important factor controlling the bubble distribution. The structure of these interfaces was characterised in terms of SGBD spacing and Burgers vector. The method used was similar to that described by Clark and Smith (194) which involves a comparison of the observed dislocation structure with a calculated dislocation network. SGBDs accomodate the deviation in misorientation from an exact coincidence relationship. Typically, three GBD arrays are necessary to accomodate this misorientation. The line direction and spacing of these GBDs can be calculated using Frank's formula if the deviation from exact coincidence is known, in an analagous way to that for constructing a low angle grain boundary (195). If the boundary contains three arrays of dislocations, with non-coplanar Burgers vectors \( \mathbf{b}_i \) (i=1-3) then Frank's formula allows the respective line directions of the dislocations, \( \mathbf{r}_i \), to be calculated as:

\[ \mathbf{r}_i = \left[ \mathbf{u} \times (\mathbf{b}_2 \times \mathbf{b}_3) \right] \mathbf{v} \]

with corresponding results for \( \mathbf{r}_2 \) and \( \mathbf{r}_3 \), where \( \mathbf{u} \) is a unit vector parallel to the misorientation axis and \( \mathbf{v} \) is a unit vector parallel to the grain boundary normal. The density of each array, \( \rho_i \), is obtained from:

\[ \rho_i = |\mathbf{v} \times (\mathbf{h}^* \mathbf{u})| \theta \]

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where
\[ b_1^* = \frac{b_2 \times b_3}{b_1 \cdot b_2 \times b_3} \]

and \( \theta \) is the rotation angle.

Practically, it is necessary to determine the deviation from coincidence in terms of a rotation \( \theta \), about an axis \( \mathbf{u} \) and also to determine the boundary normal \( \mathbf{v} \). The misorientation relationship between adjacent grains was determined by Kikuchi pattern analysis (after Young et al (196)). Kikuchi patterns give a sensitive indication of crystal orientation and analysis was aided by the construction of a Kikuchi map (figure 5.10). A computer program (NEWMIS) was used to facilitate the determination of the misorientation relationship across grain boundaries. A misorientation matrix, \( R' \) was formulated from Kikuchi patterns recorded from adjacent grains; \( R' \) specifies the rotation from one grain to the other. This experimental rotation matrix contains both the rotation leading to exact coincidence, \( R \), and the small angular deviation from exact coincidence \( R(02) \) (197) so that:

\[ R' = R(02) \cdot R \]

Since \( R' \) is measured and \( R \) is known (from tables (193)) the misorientation from exact coincidence is readily calculated. The small angular deviation about an axis \( \mathbf{u} \) is calculated from:

\[ R(02) = [a_{ij}] \quad (i=1-3, j=1-3) \]

and

\[ 2\cos\theta + 1 = a_{11} + a_{22} + a_{33} \]

and the direction of \( \mathbf{u} \) is given by:

\[ [(a_{22} - a_{23}), (a_{13} - a_{31}), (a_{21} - a_{12})] \]

Two techniques were used to determine the normal to the boundary plane. By systematic tilting in the microscope it was possible to
orient the boundary plane vertically and subsequent analysis of the associated diffraction pattern gave the boundary normal. Alternatively, the boundary normal was determined by the change in projected boundary image after a known specimen rotation in the microscope (after 196).

A computer program (LAGB) based on Frank's formula was used to calculate the dislocation content of low angle and high angle grain boundaries. In using Frank's formula it is necessary to assume three non-coplanar Burgers vectors. For low-angle grain boundaries the dislocations are normal lattice type dislocations. However, SGBDs have Burgers vectors which are translation vectors of the DSC lattice. The DSC lattice is defined as the coarsest sub-lattice of the two adjacent crystal lattices which contains all lattice points. The translation vectors are tabulated for cubic materials (193) and substitution into Frank's formula yields a calculated dislocation structure in terms of the assumed Burgers vector, line direction and spacing of three dislocation arrays.

The calculated dislocation structures for interfaces studied here were shown to be consistent with both a Burgers vector analysis and with the dislocation spacings and line directions measured from projected boundary images. Two-beam diffraction conditions using a variety of diffraction vectors were used to demonstrate consistency of diffraction contrast of the SGBDs with the direction of the assumed Burgers vector. The dislocation line directions were calculated from projected grain boundary images (figure 5.11).

The beam axis, B (from Kikuchi patterns), the projected
dislocation line direction, \( P \), and the true line direction, \( D \), all lie in a common plane with normal \( B \times P \). The normal to the boundary plane is \( N \) and the dislocation line direction is given by:

\[
D = N \times (B \times P)
\]

By recording grain boundary images with little or no specimen tilt it was possible to estimate the true dislocation spacing from (198):

\[
\frac{d}{d_p} = \frac{l^2(w^2 + t^2)}{w^2(l^2 + t^2)}
\]

Where \( l \) is the projected dislocation line length, \( w \) is the projected width and \( t \) the specimen thickness (Figure 5.11); \( d \) is the true dislocation spacing and \( d_p \) is the measured (projected) dislocation spacing.
CHAPTER SIX EXPERIMENTAL RESULTS

6.1 INTRODUCTION

Transmission electron microscopy was used to study the nucleation and growth of helium bubbles at grain boundaries after both helium ion implantation and dual-beam irradiation. The radiation induced microstructures within grains were characterised as a precursor to these studies. The density of bubbles at grain boundaries was studied as a function of grain boundary structure, gas implantation rate, temperature and dual-beam irradiation. Grain boundaries were also identified as sites for heterogeneous nucleation of dislocation loops; loops nucleate and grow at coherent twin interfaces and in the vicinity of some grain boundaries. (All tables referred to are bound together at the end of this chapter).

6.2 MICROSTRUCTURAL DEVELOPMENT WITHIN GRAINS

Irradiation induced microstructures were studied to characterise the distribution of helium bubbles within grains following both helium-ion and dual-ion irradiation. Furthermore, chromium-ion and dual-ion irradiations were used to establish the operating parameters of the dual beam facility; the microstructures were characterised and a number of limitations were identified with respect to the simulation of damage due to fusion neutrons.
6.2.1 HELIUM BUBBLES WITHIN GRAINS

Helium bubbles nucleate and grow within grains and at grain boundaries during helium-ion implantation at 600°C. Few bubbles were resolvable within grains after implantation to 1400appmHe whereas bubbles are visible at grain boundaries (Figure 6.1a). At a higher dose (3500appmHe) small (1nm radius) bubbles are resolvable within grains (Figure 6.1b). Implantation at 600°C to a mean concentration of 7000appmHe results in a higher density of visible bubbles. The distribution of bubbles is highly heterogeneous; bubbles decorate faulted dislocation loops and are often found in the vicinity of dislocations (Figure 6.2). Note how weak-beam microscopy enables the simultaneous imaging of both bubbles and dislocations whereas bright field microscopy only allows strong contrast from either dislocations (dynamical) or bubbles (kinematical). Bubbles show a bright sharp fringe in weak-beam images; this is the first thickness fringe and is sharp since the thickness gradient at the edge of a bubble is large and the effective extinction distance is small (s large). Thus the weak-beam technique enables the crisp (in-focus) imaging of both bubbles and dislocations.

The bubble density within grains was measured after 40keV helium-ion implantation at 600°C to a dose of 7000appmHe (averaged over the implanted depth). The bubble density was estimated from seven sampled regions, each with an area of $3.75\times10^{-13}m^2$. The sampled volume was estimated as $5.6\times10^{-20}m^3$ for each region by assuming a foil thickness of 150nm (the depth of the implanted region). The bubble density varied from region to region within the range $1.7\times10^{21}$ to $4.1\times10^{21}$ bubbles $m^{-3}$ which reflects the
heterogeneous bubble distribution; the mean bubble density was $3.0 \times 10^{21}$ bubbles m$^{-3}$. The bubble size was also estimated, the bubbles were assumed to be spherical. A histogram of measured bubble radii is shown in Figure 6.3; the size distribution shows a tail at high bubble radii. The mean bubble radius was 2.9 nm although the median radius of 2.5 nm may better represent the bubble size distribution. For comparison the mean radius of bubbles at grain boundaries after the same implantation dose was 2.6 nm (Section 6.3.3).

The concentration of helium present in visible bubbles was estimated. If the bubbles are assumed to be at their equilibrium size (where the pressure in the bubble is balanced by the surface tension) and if helium behaves as an ideal gas we can write:

$$n = \frac{8nYr^2}{3kT} \quad \text{6.1}$$

Where $n$ is the number of helium atoms in a bubble of radius $r$; $k$ and $T$ are Boltzmann's constant and the absolute temperature respectively and $Y$ is the surface energy ($Y = 2 \text{J m}^{-2}$ (199)). For a bubble with radius 2.5 nm, $n = 8700$. The mean bubble density is $3 \times 10^{21}$ and the concentration of helium present in visible bubbles is estimated as 290 appmHe. Thus only 4% of the implanted helium is accounted for in visible bubbles if the bubbles are at their equilibrium size.

Dual-beam irradiations were used to study effects of additional displacement damage on the size and density of bubbles within grains. Two groups of irradiations were performed both at 600°C. In the first, the displacement rate was constant (constant chromium-ion beam current) as was the displacement dose but the helium implantation rate was varied. Table 6.1 shows the implantation parameters used. Note that the He/dpa ratio varies from 200 to 1800 appmHe/dpa. The mean
bubble radius and measured bubble densities are also shown. Figure 6.4 shows representative microstructures and there were no resolvable bubbles following irradiation to a dose of 700appmHe. Histograms of measured bubble radii are shown in Figure 6.5. Note that the bubble density increases markedly with increasing He/dpa ratio whereas the mean bubble size shows a trend to higher radii.

In the second group of irradiations the helium implantation rate and helium dose were constant but the displacement rate was varied. Table 6.2 shows the irradiation parameter used. Figure 6.6 shows the bubble populations following these dual-beam irradiations and Figure 6.7 shows histograms of bubble sizes. Here, both the bubble density and bubble size decrease with increasing He/dpa ratio. The bubble density is enhanced during dual beam irradiation compared to helium-ion implantation alone, where the measured bubble density was only $3 \times 10^{21}$ bubbles m$^{-3}$. The bubble density increases with both helium implantation rate (displacement rate constant) and displacement rate (helium implantation rate constant). The effect of these parameters on the bubble radius is not clear but in general there is a small increase in bubble size with both implantation rate and displacement rate.

An estimate was made of the percentage of the implanted helium present in visible bubbles assuming the bubbles are at their equilibrium size. The estimates are shown in Table 6.3. In general, more helium is evident in bubbles following dual-beam irradiation than after helium implantation alone, but a large percentage of the implanted helium cannot be accounted for in equilibrium sized bubbles. The variation in these estimates are due to the irregular trends of
bubble size with implanted dose (Tables 6.1 and 6.2) which probably reflect the difficulties of accurately monitoring two ion-beams simultaneously (section 5.4). During dual-beam irradiation it was not possible to measure the target current of each ion-beam; the beams were monitored on collimators in front of the target (Figure 5.3). Consequently, variations in the target current of either beam may have occurred during irradiation without detection. The inability to measure each target beam current independently during dual-beam irradiation is a major limitation. However, it is clear that extra displacement damage due to a second ion-beam enhances the density and size of bubbles within grains; a larger fraction of the implanted helium can be accounted for in visible bubbles after dual-beam irradiation than after helium-ion implantation alone. Of course, the problem of current measurement does not arise during single beam irradiation because the target beam current is monitored throughout.

6.2.2 DISLOCATION DEVELOPMENT DURING IRRADIATION

High temperature ion-irradiation of austenitic alloys results in the nucleation and growth of interstitial dislocation loops (Chapter 4). In this work, Frank faulted dislocation loops were found to nucleate and grow during helium-ion, chromium-ion and dual-ion irradiation. A Burgers vector analysis was made to confirm that the loops are indeed interstitial in nature. The analysis was performed on dislocation loops which form after dual-beam irradiation at 600°C to a dose of 0.4dpa and 80ppmHe (Figure 6.8). Four sets of dislocations were identified and invisibility criteria indicate that the Burgers vectors are consistent with Frank faulted loops with \( b = a/3 \langle 111 \rangle \) (Table 6.4). The sign of each Burgers vector was
determined by the change from inside to outside contrast on change in sign of \( g \) (e.g. Figure 6.9). The interstitial nature of the loops is thus confirmed since \( \mathbf{n} \cdot \mathbf{b} > 0 \) for each set of loops (where \( \mathbf{n} \) is the upward drawn normal to the habit plane).

Table 6.5 summarises the development of dislocation microstructures during single beam chromium-ion and dual-ion irradiation. Representative micrographs are shown in figure 6.10. In general, the size of dislocation loops and the degree of unfaulting is enhanced during dual-beam irradiation relative to chromium-ion irradiation. Figure 6.10a and b show the dislocation microstructure after chromium-ion and dual-ion irradiation at 600°C to 0.4dpa. It is clear that simultaneous implantation of helium enhances the growth of dislocation loops. Dual-beam irradiation to higher displacement doses (3.7dpa) results in dislocation segments (Figure 6.10c) where the dislocation loops have unfaulted and climb to form a network. Figure 6.10d shows faulted, hexagonal loops which develop during chromium-ion irradiation to a dose of 2dpa. In marked comparison, Figure 6.10e shows both faulted and unfaulted dislocation loops which form after dual-ion irradiation to only 0.9dpa. The effect of helium on the development of interstitial dislocation loops is also shown in figure 6.2; the displacement dose due to helium-ion implantation was only 0.4dpa yet large interstitial dislocation loops developed. Irregular shaped loops developed during helium-ion implantation and dual-ion irradiation. Large faulted dislocation loops were frequently found to exhibit an irregular rosette shape (figure 6.11) rather than the circular shape typical of other loops. Chromium-ion irradiation alone resulted in hexagonal shaped loops (figure 6.10d).
6.2.3 $\textit{M}_{23}\textit{C}_6$ PRECIPITATION

A fine distribution of $\textit{M}_{23}\textit{C}_6$ precipitates was identified in samples after both chromium-ion and dual-ion irradiation at 600°C to a high dose of 26dpa. Figure 6.12a shows that the precipitation occurs on a very fine scale; the diffraction pattern shows characteristic spots from $\textit{M}_{23}\textit{C}_6$ and the austenitic matrix. $\textit{M}_{23}\textit{C}_6$ has an FCC crystal structure and the orientation relationship with the matrix is simply $[100]_{\textit{M}_{23}\textit{C}_6} \parallel [100]$ matrix; and $[110]_{\textit{M}_{23}\textit{C}_6} \parallel [110]$ matrix. The ratio of interplanar spacings is $d(\textit{M}_{23}\textit{C}_6)/d(\text{matrix})=2.95$ (200) which gives rise to the carbide spots at intervals of approximately 1/3 and 2/3 between the matrix spots in the diffraction pattern. Figure 6.12 shows recrystallisation at a grain boundary, an observation which was characteristic in these high dose specimens. The recrystallising grains appear to be free of precipitates suggesting that precipitate dissolution is the driving force for recrystallisation.

The observation of $\textit{M}_{23}\textit{C}_6$ precipitates in the ternary austenitic alloy is unexpected because the nominal carbon concentration is only 0.006%. The irradiation time for these specimens was approximately 1 hour and 40 minutes whereas the thermal precipitation of $\textit{M}_{23}\textit{C}_6$ in stainless steel is normally a slow process; at 600°C blocky precipitates first appear at grain boundaries after at least 3 hours in commercial 316 stainless steel (201) where the carbon concentration can be as high as 0.08%. It must be concluded that precipitation is radiation assisted. Boulanger reported a similar fine distribution of $\textit{M}_{23}\textit{C}_6$ precipitates in an 18%Cr,14%Ni,105ppmC austenitic alloy following irradiation with
500 keV nickel-ions in the temperature range 500-550°C (202). At higher temperatures (600-650°C) no carbides formed but irradiation induced voids were identified whereas no voids formed when carbides were present. Similarly, no voids were identified in the work reported here. The formation of a fine dispersion of $M_{23}C_6$ apparently inhibits void formation, possibly by enhanced recombination of interstitials and vacancies at the coherent matrix-precipitate interface.

The nominal carbon content in the alloy studied here is 0.006% and an additional source of carbon is needed to account for the observed $M_{23}C_6$ precipitation. Two possible sources of carbon can be identified; carbon introduced by the thermal/mechanical pretreatment and carbon contamination in the vacuum system during irradiation. Boulanger ascribed the observation to carbon contamination in the vacuum system (202). The precipitation of $M_{23}C_6$ during dual-beam irradiation sets limitations on the use of the dual-beam facility for the simulation of fusion neutron irradiation. High displacement doses should be avoided so it is not possible to simulate the He/dpa ratios expected in fusion reactor first wall materials (20appmHe/dpa). This problem and the additional limitations of point defect loss to surfaces and of self-ion injection associated with the dual-beam facility are outlined in the Appendix. Despite these limitations, the dual-beam facility was used to study the synergistic effects of helium-ion implantation and chromium-ion irradiation (appmHe/dpa>200) on helium bubble formation at low displacement doses (<10dpa) where $M_{23}C_6$ precipitates do not form.
6.3 HELIUM BUBBLES AT GRAIN BOUNDARIES

6.3.1 GENERAL OBSERVATIONS

All crystal interfaces showed preferred nucleation of helium bubbles (e.g. figure 6.1) except coherent twin boundaries where bubble nucleation was not promoted (figure 6.13). A high density of bubbles was visible at grain boundaries before any were resolved within grains. The bubble size and density varied from boundary to boundary and bubble denuded zones were clearly defined after implantation at 600°C to a dose of $2 \times 10^4$ appmHe. The denuded zones appeared symmetrical about the boundary position (figure 6.14). The size of the denuded zones were measured by counting bubbles in the vicinity of boundaries which were oriented vertically in the microscope. The region adjacent to each boundary was divided into strips 30nm wide and 500nm long and running parallel to the boundary, a total of seven strips were defined on each side of the boundary and the number of bubbles per strip was recorded. The bubble count per strip was expressed as a percentage of the total bubbles counted in the seven strips. Figure 6.15a shows the percentage of total bubble counts per strip for one grain boundary. Note that the histogram reflects the symmetrical nature of the denuded zone. Figure 6.15b shows the percentage of total counts per strip as a function of distance from the boundary, but averaged over fifteen denuded zones. The bubble density increases into the grain to an asymptotic value. By defining the width of the denuded zone as that at which the bubble density ($\%$ bubble count) is reduced to half the matrix concentration an average zone width of 50nm is found although the bubble concentration is depleted from a zone 135nm wide (Figure 6.15b).
6.3.2 THE BUBBLE DENSITY AT GRAIN BOUNDARIES

The areal density of bubbles at grain boundaries varied from boundary to boundary and was measured as a function of various parameters. These included implantation temperature, gas implantation rate and extra displacement damage (during dual-beam irradiation).

6.3.2.1 THE ROLE OF TEMPERATURE

Specimens were irradiated at 450°C, 550°C and 600°C with 70keV helium-ions at a rate of $9 \times 10^{16}$ ions m$^{-2}$s$^{-1}$ to a mean concentration of 5600appmHe. The resultant density of bubbles at grain boundaries was measured using TEM (section 5.6.1). At least fifteen grain boundaries were sampled for each irradiation temperature and the densities are shown in table 6.6. Figure 6.16 shows the mean bubble density and scatter as a function of temperature for boundaries with no resolvable dislocation structure and also shows the density of bubbles at interfaces which exhibit a resolvable array of GBDs. Micrographs showing the size and density of bubbles at grain boundaries are shown in Figure 6.17. There are three features of interest. First, for each irradiation temperature there is a range of measured bubble densities. Second, the bubble density shows a general increase with decreasing temperature; the mean bubble density at interfaces which exhibit no resolvable dislocation structure is $1.4 \times 10^{15}$m$^{-2}$ at 450°C and $1.4 \times 10^{15}$m$^{-2}$ at 600°C. Finally, the bubble density is enhanced at all temperatures by the presence of visible dislocation arrays at the interface.
6.3.2.2 THE ROLE OF GAS IMPLANTATION RATE

Specimens were irradiated with 40keV helium-ions at 600°C; the implantation rate was varied by changing the ion-beam current (Table 6.7). The density of bubbles at grain boundaries was measured for at least fifteen interfaces for each implantation rate (Table 6.8). The micrographs in figure 6.18 show the effect of implantation rate on bubble density. Figure 6.19 shows the mean bubble density and experimental scatter as a function of implantation rate. Again, the bubble density varied from boundary to boundary. Furthermore, the bubble density increased with implantation rate; the mean bubble density increased from 0.51x10^{15}m^{-2} at a rate of 1.3appmHe s^{-1} to 1.4x10^{15}m^{-2} at a rate of 6.5appmHe s^{-1}.

Additional irradiations were performed at a gas implantation rate of 3.3appmHe s^{-1} to a mean implanted concentration of only 1770appmHe. The density of bubbles measured at various grain boundaries are shown in Table 6.9. These results should be compared with column 2 of Table 6.8. Note that the mean bubble density and the range of densities are approximately the same for the low dose and high dose irradiations which indicates that bubble density is insensitive to dose.

6.3.2.3 THE ROLE OF DISPLACEMENT DAMAGE

The dual-beam facility was used to investigate the role of displacement damage on the density of bubbles at grain boundaries. The 40keV helium-ion beam currents and doses were the same as those in Table 6.7; this ensured that any effects due to gas implantation rate.
could be excluded by comparison of results with Figure 6.21 and Table 6.8. The 380keV chromium-ion beam current was 0.05μA for each irradiation to achieve approximately the same displacement dose for each irradiation condition (there is some contribution to the total dose due to the helium-ion beam). The irradiation conditions are shown in Table 6.10.

Table 6.11 shows the measured density of bubbles at grain boundaries following dual-beam irradiation; figure 6.20 shows the effect of dual-beam irradiation on the mean bubble density and on the density variation from boundary to boundary. Representative micrographs are shown in figure 6.21; note the high density of bubbles within the grains (figure 6.21b and c). To avoid confusion between bubbles at the interface and bubbles within grains each grain boundary was tilted vertically in the microscope where it was clear which bubbles were at the interface. Comparison of figure 6.20 with figure 6.19 shows that the bubble density varies with helium implantation rate but additional displacement damage during dual-beam irradiation has a minimal effect on the density of bubbles at grain boundaries. This is in marked contrast to the effect of displacement damage on the density of bubbles within grains (section 6.2.1) where the density is significantly enhanced.

6.3.3 THE SIZE OF BUBBLES AT GRAIN BOUNDARIES

For each irradiation condition studied, the density of bubbles at grain boundaries varied from interface to interface; the sizes of bubbles were found to vary in a consistent manner. The variation in bubble size was measured for samples irradiated with 40keV helium-ions
at 600°C at a gas implantation rate of 3.3appmHes⁻¹ (see Table 6.8, column 2). The bubbles were assumed to be spherical and the bubble radius was measured. A few boundaries were decorated with elongated bubbles and these were excluded from this analysis. The mean bubble radius was calculated for each grain boundary and are shown as a function of bubble density in figure 6.22. The bubble size decreases with increasing bubble density which may indicate that the concentration of helium at each grain boundary is fixed; thereby limiting the bubble size at interfaces with a high bubble density. If the bubbles are assumed to be at their equilibrium size then the concentration of helium at each interface can be calculated. Since,

\[
\frac{n}{3kT} = \frac{8\pi r^2}{3kT}
\]  

we can write,

\[
C = \rho n = \frac{\rho 8\pi r^2}{3kT}
\]  

Where \(C\) is the concentration of helium at the interface (atoms m⁻²), \(n\) is the number of helium atoms per bubble and \(\rho\) is the density of bubbles at the interface (bubbles m⁻²). If the concentration of helium is the same at all interfaces then the relationship between bubble size and bubble density is simply;

\[
r = \left(\frac{2kT}{8\pi n}\right)^{1/2} \rho^{-1/2}
\]  

Figure 6.23 shows the bubble radius as a linear function of \((\text{density})^{-1/2}\). On the basis of these assumptions it is reasonable to assume that the concentration of helium is approximately the same at all grain boundaries; in other words, the sink strength for helium is the same for all grain boundaries (except coherent twin interfaces).

In section 6.3.2 it was shown that the density of bubbles at grain boundaries is dependent on both temperature and gas implantation.
rate whereas extra displacement damage and total dose have little or no effect. The size of bubbles at grain boundaries was measured as a function of these same variables. Grain boundaries were chosen with bubble densities close to the mean density for each irradiation condition; this ensured that boundary to boundary variations were minimized. Three representative interfaces were sampled for each irradiation condition and the mean bubble radii are shown in Table 6.12. The mean radius increases with temperature and dose. The apparent increase in bubble size with implantation rate (during both single-ion and dual-ion irradiation) is essentially a dose effect. Additional displacement damage during dual-beam irradiation has little effect on the size of bubbles at grain boundaries.

An estimate was made of the arrival rate of gas atoms at grain boundaries. By comparing this arrival rate with the gas implantation rate an estimate can be made of the effective helium capture volume associated with a grain boundary. The concentration of helium was estimated using equation 6.2 (i.e. assuming equilibrium size), where the bubble size and density are shown in Table 6.12. The helium implantation rate was calculated from the helium-ion beam current (Table 5.2). The ratio of the gas arrival rate at an interface \( R_A \) \( \text{atoms m}^{-2}\text{s}^{-1} \) to the volume implantation rate \( R_I \) \( \text{atoms m}^{-3}\text{s}^{-1} \) is a measure of the width of the capture volume associated with the grain boundary. All of these estimated parameters are shown in Table 6.13 as a function of irradiation condition; the last column is the effective capture width associated with a grain boundary. The capture width increases with irradiation temperature from 9nm at 450°C to 17nm at 600°C but is relatively insensitive to helium-ion beam energy, gas implantation
rate and dual-beam irradiation, being 19.5nm+/-2.5nm for all irradiations at 600°C. This helium capture width is estimated assuming that the bubbles are at their equilibrium size and should be compared to the total width of the bubble denuded zone of 100nm (section 6.3.1).

6.3.4 BUBBLES AT GRAIN BOUNDARY DISLOCATIONS

The bubble density at grain boundaries is enhanced by the presence of resolvable dislocation arrays at the interface (e.g. Table 6.6). A number of interfaces were chosen to study the role of dislocation spacing and Burgers vector on the nucleation of helium bubbles. For consistency, all interfaces were chosen from samples irradiated at 600°C using 70keV helium-ions. The measured misorientation and boundary plane for four interfaces are shown in Table 6.14. The interfaces include a low-angle grain boundary (Figure 6.24) and three high angle grain boundaries where the misorientation is close to a coincidence relationship (Figure 6.25). The measured dislocation spacing and bubble density at these interfaces are shown in Table 6.15. For comparison, the mean bubble density at interfaces which exhibit no resolvable dislocation structure is 1.0x10^{15} m^{-2} for the irradiation conditions used here (Figure 6.16).

The low angle grain boundary exhibits three facets, two of which contain a resolvable dislocation array with a measured spacing of 12nm (facets A and B). The third facet (C) has a number of widely spaced dislocations which contribute little to the misorientation; no further structure could be resolved. The bubble density is enhanced
on facets A and B but the density at facet C is not. The dislocation spacing at facets A and B is so small that every bubble appears to lie on a dislocation (Figure 6.24). Figure 6.26 shows an extension of facet A where the boundary plane changes. Here, the dislocation spacing is much larger and bubbles decorate both the visible dislocations and the unresolved interfacial structure between them.

The three high angle grain boundaries are close to Σ3, Σ29a and Σ43a misorientations (Table 6.14). Each interface exhibits one coarse dislocation array with measured spacings as shown in Table 6.15. The dislocation spacing in the Σ29a related interface changes to accommodate the change in boundary plane (Figure 6.25). Helium bubbles are clearly aligned along the GBDs in these interfaces and the measured bubble densities are shown in Table 6.15; the presence of visible GBDs is associated with a high density of bubble nucleation sites. Secondary GBDs accommodate the deviation in misorientation from exact coincidence (Table 6.14) and possible Burgers vectors of these dislocations can be derived from the appropriate DSC lattice (193). Franks' formula was used to calculate possible dislocation structures for the low-angle and the high-angle grain boundaries from the measured grain boundary crystallography and from assumed Burgers vectors.

For the low-angle interface it was assumed that dislocations were lattice type with Burgers vector \( b = a/2<110> \). Combinations of these lattice dislocations were used in Frank's formula to calculate the dislocation content of facets A, B and C (Figure 6.24). The solutions for each interface were dependent on the chosen combinations of Burgers vector and a number of solutions were consistent with the
observed dislocation spacing and line direction (Table 6.16).

Possible Burgers vectors of the visible dislocation arrays in facets A and B were \(a/2[01\bar{1}]\), \(a/2[10\bar{1}]\) and \(a/2[110]\). A Burgers vector analysis showed that the dislocations exhibit either no contrast or only residual contrast with the operating diffraction vectors \(g=\overline{111}\), \(g=220\) and \(g=11\overline{1}\) which is consistent with \(b=a/2[110]\) since \(g\cdot b=0\) but \(g\cdot bxu\neq 0\) for each diffraction condition (Table 6.17).

The calculated structure for facet C was also dependent on the choice of Burgers vectors. A number of solutions each gave three dislocation arrays all with spacings <5nm, which is consistent with TEM observation since any dislocation structure was irresolvable. The coarse array of dislocations in this interface was invisible with \(g=\overline{111}\), \(g=220\) and \(g=11\overline{1}\) indicating lattice type dislocations with \(b=a/2[110]\). This observation is consistent with the dislocations being extrinsic in nature.

The secondary GBDs at the three high-angle interfaces (Figure 6.25) were assumed to have Burgers vectors which are translation vectors of the appropriate DSC lattice. In each case, three sets of dislocations are necessary to account for the measured misorientation from exact coincidence. However, the general solution for all the high angle interfaces requires one coarse array of dislocations with large Burgers vector (\(b_3\)-type) and two further arrays with small Burgers vector with spacing <4nm. The calculations show that only the \(b_3\)-type dislocation arrays should be visible in the TEM, as was observed. The Burgers vector of the \(b_3\)-dislocations are tabulated (Table 6.18). Table 6.16 shows good agreement between the measured and calculated dislocation spacings and line directions. The
calculated dislocation spacings for both sections of the $\Sigma_{29a}$ interface are about 50% of the calculated values. This error may be due to errors in the determination of the misorientation from exact coincidence, or may be due to the occurrence of multiple DSC vectors. The calculated spacings do reflect the observed coarsening of the dislocation array from section A to section B of the interface (Figure 6.25). A diffraction analysis was performed on the dislocation arrays in the $\Sigma_3$, $\Sigma_{29a}$ and $\Sigma_{43a}$ related interfaces. The analysis (Table 6.19) was consistent with $b_3$-type SGBDs with relatively large Burgers vectors (Table 6.18).

In summary, the dislocation content of the low-angle interface is consistent with lattice type Burgers vectors. The observed dislocation content in the high-angle grain boundaries is consistent with $b_3$-type SGBDs where the magnitude of the Burgers vector is $|b|>0.26a$. The bubble density is enhanced where there are resolvable dislocations present in the interface; bubbles are clearly aligned along the SGBDs. Bubble alignment along GBDs was also evident at lower irradiation temperatures (Figure 6.27) but no dislocation analysis was performed. Of particular interest is the interface shown in figure 6.27 b and c. This specimen was irradiated at 450°C to a dose of 6100appmHe. The bright-field micrograph shows a high density of small bubbles at the interface; the bubbles show no alignment along the coarse dislocation array (in weak contrast). The dark-field micrograph shows a second dislocation array. Projection of the bubble image onto the dislocation image shows that a high proportion of the bubbles decorate the fine dislocation array.

Additional structural features were found to control the
distribution of bubbles at incoherent twin interfaces. Figure 6.28 shows a pair of bright-field and dark-field micrographs of an incoherent twin interface. The bright-field image shows bubbles associated with regions which exhibit dark contrast. The contrast is reversed in dark-field and the bubble distribution is more clearly shown. Bubbles are also associated with the line defects which separate the regions of black/white contrast. By tilting the interface vertically in the microscope the regions of black/white contrast are shown to be coplanar. The origin of this contrast effect is not clear but is given consideration in the next chapter.

Not all incoherent twin interfaces exhibit marked black/white contrast. Figure 6.29 shows three micrographs of the same incoherent twin interface. A high density of bubbles is evident and features of interest are the small steps which delineate different facets of the interface (figure 6.29a) and the dislocations which are visible with an operating diffraction vector $g=220$. Stereomicroscopy revealed the presence of small steps which were decorated with bubbles. There is no clear alignment of bubbles along the dislocations which are visible in Figure 6.29c. Diffraction analysis showed the dislocations to be invisible with $g=11\bar{1}$, $g=02\bar{2}$ and $g=200$. It is thus reasonable to conclude that the dislocations are extrinsic in nature with Burgers vector $\mathbf{b}=a/2[01\bar{1}]$. These dislocations are not structural GBDs and it is not clear that they were present during irradiation. From the numerous boundaries studied there is no evidence which demonstrates the alignment of bubbles along extrinsic GBDs. This is in marked contrast to the case for intrinsic SGBDs where bubble alignment is apparent.
Grain boundaries act as preferential nucleation sites for helium bubbles. Two additional effects of radiation at grain boundaries were studied; both involve the heterogeneous nucleation and growth of interstitial dislocation loops. Loops nucleate preferentially at coherent twin interfaces and in the immediate vicinity of some grain boundaries.

6.4.1 DISLOCATION LOOPS AT TWIN BOUNDARIES

Dislocation loops were found to nucleate and grow at (111) coherent twin interfaces during both chromium-ion and dual-ion irradiation at 600°C. This is in marked contrast to the nucleation of helium bubbles where the coherent twin interface was the only crystal interface which did not exhibit preferential bubble nucleation. Figure 6.30 shows the shape of dislocation loops which nucleate at the twin boundaries. Chromium-ion irradiation alone (0.4dpa) produces loops which are approximately triangular in shape whereas dual-beam irradiation results in irregular shaped loops. After dual-beam irradiation to 0.4dpa (200appmHe/dpa) the smaller loops appear triangular but the larger loops show three extended lobes. The large loops which develop after 3.5dpa (200appmHe/dpa) are also irregular in shape and occupy a much larger fraction of the interface. Some of the loops exhibit three extended lobes whereas others have coalesced to form irregular shapes.

A Burgers vector analysis was made to determine the interstitial/vacancy nature of the loops. This analysis was made on the loops shown in figure 6.30. The common-g technique was used to
ensure similar diffraction conditions in both the twin and matrix
grains and any additional contrast due to the interface was avoided.
In order to achieve low values of $g \cdot b$ the chosen common vectors were
\(<220>\) type, which are parallel to the twin plane and \(<311>\) type, which
are not. The dislocation loops were invisible with $g=+/-[220]$, $g=+/-[202]$ and $g=+/[-022]$ (e.g. Figure 6.31); the Burgers vector
must be normal to the twin plane and is likely to be $b=a/3[111]$, which
is a translation vector of the $\Sigma 3$ DSC lattice. The sign of the
Burgers vector defines the vacancy/interstitial nature of the loops
and was determined by the change in inside/outside contrast of the
dislocation image with change in sign of the diffraction vector. This
analysis was made using matrix diffraction vectors $g=+/[131]
(\overline{311}_{\text{TWIN}})$ and $g=+/[311] (1 \overline{3} 3_{\text{TWIN}})$. The loops were imaged with
the beam axis close to the $[125]$ matrix pole. Figure 6.32 shows the
change from inside to outside contrast with change in sign of $g$, note
the apparent change in the width of the lobes. The Burgers vector was
shown to be $b=a/3[111]$ since the loops exhibit outside contrast with
$g=131$ and $g=311$. Furthermore, since the loops lie on the $<111>$ twin
plane they are interstitial in nature.

The crystallography of the dislocation loops at twins is shown in
Figure 6.33; the sides of triangular loops lie along the $<110>$
directions and the lobes of the three-lobed loops extend in the $<211>$
directions. Nucleation and growth of interstitial dislocation loops
at twin interfaces is associated with marked denudation of dislocation
loops in the matrix. Figure 6.34b shows the early stages of loop
denudation and Figure 6.34a shows the denuded zone associated with the
interface in Figure 6.30b.
6.4.2 HETEROGENEOUS LOOP NUCLEATION NEAR GRAIN BOUNDARIES

Interstitial dislocation loops nucleate heterogeneously at (111) coherent twin interfaces. Further heterogeneous loop nucleation was observed adjacent to some grain boundaries. Figure 6.35a shows nucleation of small dislocation loops in the vicinity of a grain boundary following irradiation with 380keV chromium-ions at 600°C to a displacement dose of 0.4dpa. By tilting the specimen in the microscope it was shown that the loops nucleate on one side of the boundary at a range of 15-30nm from the interface (Figure 6.35b). The high density of loop nucleation adjacent to the boundary was uncharacteristic of loop nucleation within the grain. Five boundaries were identified in this specimen which showed a similarly high density of loops on one side of the interface. None of these interfaces were close to a coincident site misorientation but, in each case, one of the grains adjacent to the boundary (the one without the loops) was oriented such that the foil normal was parallel to a <110> direction. Stereo microscopy showed that the distribution of loops relative to the grain boundary and the ion-beam direction was as shown in Figure 6.36. The dislocation loops were found to nucleate below the grain boundary with respect to the direction of the incident ion-beam.

A Burgers vector analysis (Table 6.20) identified three sets of loops as interstitial in nature and both faulted and unfaulted loops were present. The Burgers vector and nature of other loops were not determined unambiguously.
Transmission electron microscopy was used to characterise the effects of helium-ion and dual-ion irradiation on the microstructure of an austenitic alloy. Grain boundaries were identified as sites for the preferential nucleation of helium bubbles. Heterogeneous nucleation of interstitial dislocation loops was observed both at coherent twin interfaces and in the vicinity of some grain boundaries. The experimental results can be summarised:

1. Helium-ion implantation of the austenitic alloy in the temperature range 450°C to 600°C results in the nucleation and growth of helium bubbles both at grain boundaries and within grains. Bubbles are visible at grain boundaries before there are any resolvable bubbles within grains. It is not possible to account for all the implanted helium if the bubbles are at their equilibrium size and pressure.

2. All crystal interfaces exhibit preferential nucleation of helium bubbles except coherent twin interfaces. The nucleation and growth of helium bubbles at grain boundaries is associated with zones denuded of bubbles which are 50nm wide on each side of grain boundaries after helium-ion implantation at 600°C.

3. Dual-beam irradiation results in higher densities of helium bubbles within grains compared to helium-ion implantation alone. The bubble density increases as a function of both gas implantation rate and displacement rate. In marked contrast to the formation of bubbles within grains, dual-beam irradiation has little effect on either the size or the density of bubbles at grain boundaries.

4. The density of helium bubbles varies from boundary to boundary. For each irradiation condition studied the mean bubble density at
grain boundaries varies as a function of implantation temperature and helium implantation rate.

5. The presence of resolvable arrays of GBDs at interfaces enhances the density of bubbles at grain boundaries; bubbles are aligned along resolvable SGBDs.

6. Interstitial dislocation loops nucleate and grow heterogeneously both at coherent twin interfaces and adjacent to some grain boundaries. The shape of loops at coherent twin boundaries varies as a function of irradiation conditions, being triangular after chromium-ion irradiation alone but irregular (three-lobed) in shape after dual-beam irradiation. Interstitial dislocation loops also nucleate within grains. The implantation of helium (either alone or during dual-beam irradiation) apparently enhances the size of dislocation loops and the degree of unfaulting compared to chromium-ion irradiation alone. The shape of dislocation loops within grains is also influenced by the presence of helium; faulted loops are approximately hexagonal after chromium-ion irradiation whereas circular and rosette-shaped loops develop during helium-ion and dual-ion irradiation.
TABLE 6.1
The effect of dual-beam irradiation on the size and density of helium bubbles within grains; displacement rate constant.
(displacement rate approximately $3.5 \times 10^{-3} \text{ dpa s}^{-1}$).

<table>
<thead>
<tr>
<th>TOTAL DISPLACEMENT DOSE (dpa)</th>
<th>IMPLANTED HELIUM CONCENTRATION (appmHe/dpa)</th>
<th>He/dpa RATIO</th>
<th>MEAN BUBBLE RADIUS (nm)</th>
<th>MEAN BUBBLE DENSITY ($x10^{21} \text{ m}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>700</td>
<td>200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.6</td>
<td>1400</td>
<td>390</td>
<td>1.3</td>
<td>3.9</td>
</tr>
<tr>
<td>3.7</td>
<td>3500</td>
<td>950</td>
<td>2.4</td>
<td>8.1</td>
</tr>
<tr>
<td>3.9</td>
<td>7000</td>
<td>1800</td>
<td>2.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

TABLE 6.2
Irradiation parameters used for dual-beam irradiations.
(helium dose constant at 3500appm).

<table>
<thead>
<tr>
<th>DISPLACEMENT RATE (dpa/s)</th>
<th>TOTAL DISPLACEMENT DOSE (dpa)</th>
<th>appmHe/dpa RATIO</th>
<th>MEAN BUBBLE RADIUS (nm)</th>
<th>MEAN BUBBLE DENSITY ($x10^{21} \text{ m}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.8 \times 10^{-3}$</td>
<td>0.9</td>
<td>3900</td>
<td>2.0</td>
<td>4.3</td>
</tr>
<tr>
<td>$1.5 \times 10^{-3}$</td>
<td>1.6</td>
<td>2200</td>
<td>1.1</td>
<td>5.2</td>
</tr>
<tr>
<td>$3.4 \times 10^{-3}$</td>
<td>3.7</td>
<td>950</td>
<td>2.4</td>
<td>8.1</td>
</tr>
</tbody>
</table>

TABLE 6.3
Estimated percentage of implanted helium present in visible bubbles after dual-beam irradiation.

<table>
<thead>
<tr>
<th>IMPLANTED HELIUM CONCENTRATION (appm)</th>
<th>appmHe/dpa RATIO</th>
<th>% OF IMPLANTED HELIUM IN VISIBLE BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>390</td>
<td>7</td>
</tr>
<tr>
<td>3500</td>
<td>950</td>
<td>21</td>
</tr>
<tr>
<td>7000</td>
<td>1800</td>
<td>11</td>
</tr>
<tr>
<td>3500</td>
<td>3900</td>
<td>8</td>
</tr>
<tr>
<td>3500</td>
<td>2200</td>
<td>3</td>
</tr>
</tbody>
</table>
### TABLE 6.4
\begin{tabular}{lll}

<table>
<thead>
<tr>
<th>LOOP TYPE</th>
<th>INVISIBILITY CRITERIA ($g$)</th>
<th>BURGERS VECTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2(\overline{2}0), 022</td>
<td>(a/3[\overline{1}11])</td>
</tr>
<tr>
<td>B</td>
<td>2(20), 022</td>
<td>(a/3[\overline{1}11])</td>
</tr>
<tr>
<td>C</td>
<td>2(20), 2(0)</td>
<td>(a/3[\overline{1}11])</td>
</tr>
<tr>
<td>D</td>
<td>2(20), 2(0)</td>
<td>(a/3[\overline{1}11])</td>
</tr>
</tbody>
</table>
\end{tabular}

### TABLE 6.5a
Dislocation microstructure after chromium-ion irradiation (pre-thinned foils).

\begin{tabular}{lll}

<table>
<thead>
<tr>
<th>IRRADIATION TEMPERATURE (°C)</th>
<th>DISPLACEMENT DOSE (dpa)</th>
<th>DISLOCATION MICROSTRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>4</td>
<td>Faulted interstitial loops</td>
</tr>
<tr>
<td>600</td>
<td>0.4</td>
<td>Small unidentified loops</td>
</tr>
<tr>
<td>600</td>
<td>2</td>
<td>Faulted interstitial loops</td>
</tr>
<tr>
<td>650</td>
<td>4</td>
<td>Dislocation network and some loops</td>
</tr>
</tbody>
</table>
\end{tabular}

### TABLE 6.5b
Dislocation microstructure after dual-beam irradiation at 600°C

\begin{tabular}{lllll}

<table>
<thead>
<tr>
<th>DISPLACEMENT DOSE (dpa)</th>
<th>IMPLANTED GAS (appm)</th>
<th>He/dpa RATIO</th>
<th>DISLOCATION MICROSTRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>* 0.4</td>
<td>80</td>
<td>200</td>
<td>Faulted loops</td>
</tr>
<tr>
<td>* 2</td>
<td>410</td>
<td>200</td>
<td>Faulted loops</td>
</tr>
<tr>
<td>3.5</td>
<td>700</td>
<td>200</td>
<td>Faulted and unfaulted loops</td>
</tr>
<tr>
<td>6.3</td>
<td>1300</td>
<td>200</td>
<td>Faulted and unfaulted loops</td>
</tr>
<tr>
<td>0.9</td>
<td>3500</td>
<td>3900</td>
<td>Faulted and unfaulted loops</td>
</tr>
<tr>
<td>1.6</td>
<td>3500</td>
<td>2200</td>
<td>Faulted and unfaulted loops</td>
</tr>
<tr>
<td>7.2</td>
<td>3500</td>
<td>490</td>
<td>Mainly unfaulted loops</td>
</tr>
<tr>
<td>3.6</td>
<td>1400</td>
<td>390</td>
<td>Faulted loops and segments</td>
</tr>
<tr>
<td>3.7</td>
<td>3500</td>
<td>950</td>
<td>Mainly dislocation segments</td>
</tr>
<tr>
<td>3.9</td>
<td>7000</td>
<td>1800</td>
<td>Mainly dislocation segments</td>
</tr>
</tbody>
</table>
\end{tabular}

* indicates pre-thinned foils.
### TABLE 6.6
The effect of temperature on the density of bubbles at grain boundaries.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Number of Bubbles</th>
<th>Boundary Bubble Area Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td></td>
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<table>
<thead>
<tr>
<th>Temperature</th>
<th>Number of Bubbles</th>
<th>Boundary Bubble Area Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C</td>
<td></td>
<td></td>
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<tr>
<td>550°C</td>
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</tr>
<tr>
<td>600°C</td>
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<thead>
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<th>Temperature</th>
<th>Number of Bubbles</th>
<th>Boundary Bubble Area Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td></td>
<td></td>
</tr>
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</table>

* indicates those interfaces with resolvable dislocation structure.
TABLE 6.7
Gas implantation rate as a function of helium-ion beam current.

<table>
<thead>
<tr>
<th>TARGET BEAM CURRENT µA</th>
<th>IMPLANTATION RATE appmHe/s</th>
<th>MEAN IMPLANTED CONCENTRATION appmHe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.3</td>
<td>1400</td>
</tr>
<tr>
<td>0.25</td>
<td>3.3</td>
<td>3500</td>
</tr>
<tr>
<td>0.50</td>
<td>6.5</td>
<td>7000</td>
</tr>
</tbody>
</table>

TABLE 6.8
The effect of helium-ion implantation rate on the density of bubbles at grain boundaries (implantation at 600°C).

<table>
<thead>
<tr>
<th>IMPLANTATION RATE 1.3appmHe/s</th>
<th>IMPLANTATION RATE 3.3appmHe/s</th>
<th>IMPLANTATION RATE 6.5appmHe/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>NUMBER BOUNDARY BUBBLE OF AREA DENSITY</td>
<td>NUMBER BOUNDARY BUBBLE OF AREA DENSITY</td>
<td>NUMBER BOUNDARY BUBBLE OF AREA DENSITY</td>
</tr>
<tr>
<td>10 m 10 m</td>
<td>10 m 10 m</td>
<td>10 m 10 m</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number</th>
<th>1.5</th>
<th>0.31</th>
<th>66</th>
<th>1.5</th>
<th>0.44</th>
<th>212</th>
<th>2.4</th>
<th>0.88</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>1.1</td>
<td>0.33</td>
<td>69</td>
<td>1.5</td>
<td>0.46</td>
<td>153</td>
<td>1.6</td>
<td>0.96</td>
</tr>
<tr>
<td>46</td>
<td>1.2</td>
<td>0.38</td>
<td>97</td>
<td>1.8</td>
<td>0.54</td>
<td>146</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>59</td>
<td>1.5</td>
<td>0.39</td>
<td>74</td>
<td>1.3</td>
<td>0.57</td>
<td>111</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>47</td>
<td>1.2</td>
<td>0.39</td>
<td>94</td>
<td>1.6</td>
<td>0.59</td>
<td>116</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>62</td>
<td>1.5</td>
<td>0.41</td>
<td>97</td>
<td>1.6</td>
<td>0.61</td>
<td>170</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>60</td>
<td>1.4</td>
<td>0.43</td>
<td>80</td>
<td>1.1</td>
<td>0.73</td>
<td>150</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>50</td>
<td>1.1</td>
<td>0.45</td>
<td>125</td>
<td>1.7</td>
<td>0.74</td>
<td>163</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>63</td>
<td>1.1</td>
<td>0.57</td>
<td>75</td>
<td>1.0</td>
<td>0.75</td>
<td>292</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>86</td>
<td>1.4</td>
<td>0.61</td>
<td>122</td>
<td>1.5</td>
<td>0.81</td>
<td>194</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>95</td>
<td>1.5</td>
<td>0.63</td>
<td>104</td>
<td>1.2</td>
<td>0.87</td>
<td>175</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>67</td>
<td>1.0</td>
<td>0.67</td>
<td>141</td>
<td>1.5</td>
<td>0.94</td>
<td>246</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>137</td>
<td>1.9</td>
<td>0.72</td>
<td>170</td>
<td>1.7</td>
<td>1.0</td>
<td>207</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>134</td>
<td>1.7</td>
<td>0.79</td>
<td>182</td>
<td>1.6</td>
<td>1.1</td>
<td>290</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>118</td>
<td>1.2</td>
<td>0.98*</td>
<td>134</td>
<td>1.1</td>
<td>1.2</td>
<td>202</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>197</td>
<td>1.5</td>
<td>1.3</td>
<td>281</td>
<td>1.5</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>273</td>
<td>2.0</td>
<td>1.4</td>
<td>301</td>
<td>1.5</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* interface with resolvable dislocation structure.
<table>
<thead>
<tr>
<th>NUMBER BOUNDARY BUBBLE OF AREA DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>10⁻¹³ m 10⁻¹⁵ m</td>
</tr>
<tr>
<td>55  1.2  0.46</td>
</tr>
<tr>
<td>49  0.99  0.49</td>
</tr>
<tr>
<td>73  1.3  0.49</td>
</tr>
<tr>
<td>86  1.4  0.61</td>
</tr>
<tr>
<td>78  1.2  0.65</td>
</tr>
<tr>
<td>131 2.0  0.66</td>
</tr>
<tr>
<td>81  1.2  0.68</td>
</tr>
<tr>
<td>83  1.2  0.69</td>
</tr>
<tr>
<td>90  1.3  0.69</td>
</tr>
<tr>
<td>104 1.5  0.69</td>
</tr>
<tr>
<td>77  1.1  0.70</td>
</tr>
<tr>
<td>102 1.4  0.73</td>
</tr>
<tr>
<td>132 1.7  0.78</td>
</tr>
<tr>
<td>124 1.5  0.83</td>
</tr>
<tr>
<td>129 1.5  0.86</td>
</tr>
<tr>
<td>185 1.9  0.97</td>
</tr>
<tr>
<td>164 1.5  1.1</td>
</tr>
<tr>
<td>134 1.1  1.2</td>
</tr>
<tr>
<td>230 1.9  1.2</td>
</tr>
</tbody>
</table>
### TABLE 6.10
Irradiation parameters used during dual-beam irradiation for the determination of grain boundary bubble densities.

<table>
<thead>
<tr>
<th>HELIUM-ION BEAM CURRENT (µA)</th>
<th>CHROMIUM-ION BEAM CURRENT (µA)</th>
<th>HELIUM CONCENTRATION (appm)</th>
<th>TOTAL DISPLACEMENT DOSE (dpa)</th>
<th>RATIO appmHe/dpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.05</td>
<td>1400</td>
<td>3.6</td>
<td>390</td>
</tr>
<tr>
<td>0.25</td>
<td>0.05</td>
<td>3500</td>
<td>3.7</td>
<td>950</td>
</tr>
<tr>
<td>0.50</td>
<td>0.05</td>
<td>7000</td>
<td>3.9</td>
<td>1800</td>
</tr>
</tbody>
</table>

### TABLE 6.11
The density of bubbles at grain boundaries after dual-beam irradiation at 600°C.

<table>
<thead>
<tr>
<th>DUAL-BEAM IRRADIATION</th>
<th>NUMBER BOUNDARY BUBBLE OF AREA DENSITY</th>
<th>DUAL-BEAM IRRADIATION</th>
<th>NUMBER BOUNDARY BUBBLE OF AREA DENSITY</th>
<th>DUAL-BEAM IRRADIATION</th>
<th>NUMBER BOUNDARY BUBBLE OF AREA DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>390appmHe/dpa</td>
<td>10^{-13} 2 10^{-15} m²</td>
<td>950appmHe/dpa</td>
<td>10^{-13} 2 10^{-15} m²</td>
<td>1800appmHe/dpa</td>
<td>10^{-13} 2 10^{-15} m²</td>
</tr>
</tbody>
</table>

| NUMBER BOUNDARY BUBBLES | 16 | 1.0 | 0.16 | 49 | 1.2 | 0.41 | 80 | 1.4 | 0.57 |
| NUMBER BOUNDARY BUBBLES | 18 | 1.0 | 0.18 | 51 | 1.2 | 0.43 | 90 | 1.1 | 0.82 |
| NUMBER BOUNDARY BUBBLES | 15 | 0.51 | 0.29 | 76 | 1.4 | 0.54 | 113 | 1.3 | 0.87 |
| NUMBER BOUNDARY BUBBLES | 46 | 1.0 | 0.46 | 70 | 1.2 | 0.58 | 113 | 1.0 | 1.1 |
| NUMBER BOUNDARY BUBBLES | 32 | 0.64 | 0.50 | 67 | 1.1 | 0.61 | 135 | 1.2 | 1.1 |
| **                       | 75 | 0.96 | 0.78 | 53 | 0.43 | 1.2 |
| **                       | 59 | 0.67 | 0.88 | 140 | 1.2 | 1.2 |
| **                       | 116 | 1.2 | 0.97 | 129 | 0.96 | 1.3 |
| **                       | 137 | 1.2 | 1.1 | 103 | 0.72 | 1.4 |
| **                       | 124 | 1.1 | 1.1 | 106 | 0.75 | 1.4 |
| **                       | 197 | 1.6 | 1.2 | 169 | 1.1 | 1.5 |
| **                       | 164 | 1.3 | 1.3 | 50 | 0.34 | 1.5 |
| **                       | 162 | 1.2 | 1.4 | 136 | 0.85 | 1.6 |
| **                       | 84 | 0.61 | 1.4 | 154 | 0.80 | 1.9 |
| **                       | 173 | 1.1 | 1.6 | 298 | 1.1 | 2.7* |
| **                       | 177 | 1.1 | 1.6 |

* interface with resolvable dislocation array
** only five interfaces analysed due to contamination
TABLE 6.12
The effect of irradiation parameters on the size and density of bubbles at grain boundaries.

<table>
<thead>
<tr>
<th>IRRADIATION PARAMETERS</th>
<th>MEAN BUBBLE RADIUS (nm)</th>
<th>MEAN BUBBLE DENSITY ($10^{15}$ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70keV helium-ion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.8appmHe/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td>550</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>600</td>
<td>2.7</td>
<td>1.0</td>
</tr>
<tr>
<td>40keV helium-ions at 600°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3appmHe/s (1400appm)</td>
<td>1.8</td>
<td>0.54</td>
</tr>
<tr>
<td>3.3appmHe/s (3500appm)</td>
<td>2.2</td>
<td>0.83</td>
</tr>
<tr>
<td>6.5appmHe/s (7000appm)</td>
<td>2.6</td>
<td>1.4</td>
</tr>
<tr>
<td>3.3appmHe/s (1770appm)</td>
<td>1.7</td>
<td>0.77</td>
</tr>
<tr>
<td>Dual-beam irradiation at 600°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium implantation rate:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3appmHe/s</td>
<td>1.2</td>
<td>0.31</td>
</tr>
<tr>
<td>3.3appmHe/s</td>
<td>2.2</td>
<td>0.99</td>
</tr>
<tr>
<td>6.5appmHe/s</td>
<td>2.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>
TABLE 6.13
Estimation of the capture volume associated with grain boundaries.

<table>
<thead>
<tr>
<th>IRRADIATION PARAMETERS</th>
<th>HELIUM CONC. AT GRAIN-BOUNDARIES x10^18 atoms m^-2</th>
<th>#R_A</th>
<th>#R_I</th>
<th>#R_A/R_I (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70keV helium-ion 4.8appmHe/s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>5.3</td>
<td>4.1</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>550</td>
<td>7.1</td>
<td>5.6</td>
<td>4.5</td>
<td>12</td>
</tr>
<tr>
<td>600</td>
<td>10</td>
<td>7.8</td>
<td>4.5</td>
<td>17</td>
</tr>
</tbody>
</table>

| 40keV helium-ions at 600°C. | 1.3appmHe/s (1400appm) | 2.4 | 2.2 | 1.2 | 18 |
|                            | 3.3appmHe/s (3500appm) | 5.6 | 5.1 | 3.0 | 17 |
|                            | 6.5appmHe/s (7000appm) | 15  | 12  | 6.0 | 20 |

| 3.3appmHe/s (1770appm)     | 3.1                                           | 5.7  | 3.0  | 19 |

| Dual-beam irradiation at 600°C. Helium implantation rate: | 1.3appmHe/s | 0.62 | 0.57 | 1.2 | 5* |
|                                                             | 3.3appmHe/s | 6.6  | 6.1  | 3.0 | 20 |
|                                                             | 6.5appmHe/s | 14   | 13   | 3.0 | 22 |

#

R_A = helium atom arrival rate at grain boundaries.
(x10^15 atoms/m^2/s)

R_I = helium atom implantation rate.
(x10^23 atoms/m^2/s)

R_A/R_I is in units of nanometers and represents the width of the capture volume at grain boundaries.

* Discrepancy due to low helium beam current during implantation. A limited number of interfaces were sampled.
TABLE 6.14
Boundary crystallography of a low-angle and three high angle grain boundaries.

<table>
<thead>
<tr>
<th>LOW-ANGLE INTERFACE FACET A</th>
<th>MEASURED MISORIENTATION</th>
<th>NEAREST COINCIDENCE MISORIENTATION</th>
<th>DEVIATION FROM COINCIDENCE</th>
<th>BOUNDARY PLANE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.8° about</td>
<td>-</td>
<td>-</td>
<td>(2 1 0)</td>
</tr>
<tr>
<td>LOW-ANGLE INTERFACE FACET B</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>(1 2 4)</td>
</tr>
</tbody>
</table>

\[ \Sigma 3 \]
57.7° about 60.0° about 2.6° about (0.44 0.56 1.0)
[1.0 1.03 0.98] [1 1 1] [0.73 0.13 0.67]

\[ \Sigma 29a \]
43.2° about 43.6° about 3.5° about (5 11 15)
[0.08 1.0 0.02] [0 1 0] [0.83 0.17 0.54]

\[ \Sigma 43a \]
13.5° about 15.2° about 1.9° about (0.78 0.93 1.0)
[1.0 1.16 1.17] [1 1 7] [0.89 0.39 0.23]

TABLE 6.15
The measured dislocation spacing and bubble density at a low-angle and three high angle grain boundaries.

<table>
<thead>
<tr>
<th>INTERFACE</th>
<th>MEASURED DISLOCATION SPACING</th>
<th>BUBBLE DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-angle facet A</td>
<td>12</td>
<td>1.8</td>
</tr>
<tr>
<td>Low-angle facet B</td>
<td>12</td>
<td>1.6</td>
</tr>
<tr>
<td>Low-angle facet C</td>
<td>coarse array only</td>
<td>0.59</td>
</tr>
<tr>
<td>[ \Sigma 3 ]-related</td>
<td>22</td>
<td>1.7</td>
</tr>
<tr>
<td>[ \Sigma 29a ] section A</td>
<td>12</td>
<td>2.0</td>
</tr>
<tr>
<td>[ \Sigma 29a ] section B</td>
<td>29</td>
<td>1.5</td>
</tr>
<tr>
<td>[ \Sigma 43a ]-related</td>
<td>10</td>
<td>2.3</td>
</tr>
</tbody>
</table>
TABLE 6.16
Comparison of experimental and calculated dislocation arrays.

<table>
<thead>
<tr>
<th>DISLOCATION BOUNDARY SPACING (nm)</th>
<th>DISLOCATION-LINE DIRECTION MEAS.</th>
<th>DISLOCATION-LINE DIRECTION CALC.</th>
<th>ANGULAR* DEVIATION (DEGREES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAGB 12</td>
<td>[0.34 0.68 0.65]</td>
<td>[0.35 0.66 0.63]</td>
<td>1.5</td>
</tr>
<tr>
<td>LAGB B 12</td>
<td>[0.98 0.13 0.18]</td>
<td>[0.97 0.20 0.14]</td>
<td>4.7</td>
</tr>
<tr>
<td>Σ3 22</td>
<td>[0.68 0.47 0.56]</td>
<td>[0.59 0.56 0.58]</td>
<td>7.7</td>
</tr>
<tr>
<td>Σ29a A 12</td>
<td>[0.85 0.24 0.46]</td>
<td>[0.80 0.32 0.50]</td>
<td>8.3</td>
</tr>
<tr>
<td>Σ29a B 29</td>
<td>[0.61 0.74 0.28]</td>
<td>[0.41 0.88 0.24]</td>
<td>14.2</td>
</tr>
<tr>
<td>43a 10</td>
<td>[0.78 0.18 0.60]</td>
<td>[0.79 0.23 0.57]</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*Angle between measured (MEAS.) and calculated (CALC.) dislocation line directions.

TABLE 6.17
Diffraction conditions under which the dislocation arrays in the low-angle interface show residual contrast only.

<table>
<thead>
<tr>
<th>DIFFRACTION VECTOR</th>
<th>FACET A (u=[0.34 0.58 0.65])</th>
<th>FACET B (u=[0.98 0.13 0.18])</th>
</tr>
</thead>
<tbody>
<tr>
<td>g·bxu</td>
<td>g·bxu</td>
<td>g·bxu</td>
</tr>
<tr>
<td>Σ1Σ1</td>
<td>0.14</td>
<td>0.38</td>
</tr>
<tr>
<td>220</td>
<td>1.3</td>
<td>0.36</td>
</tr>
<tr>
<td>1Σ1</td>
<td>1.2</td>
<td>0.74</td>
</tr>
</tbody>
</table>
### TABLE 6.18
Burgers vectors of $b_3$-type dislocations for the $\Sigma 3$, $\Sigma 29a$ and $\Sigma 43a$ related boundaries.

<table>
<thead>
<tr>
<th>BOUNDARY</th>
<th>BURGERS VECTOR OF $b_3$-TYPE DISLOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma 3$</td>
<td>$a/3[111]$</td>
</tr>
<tr>
<td>$\Sigma 29a$</td>
<td>$a/58[\overline{2} 29 5]$</td>
</tr>
<tr>
<td>$\Sigma 43a$</td>
<td>$a/86[33 27 26]$</td>
</tr>
</tbody>
</table>

### TABLE 6.19
Diffraction contrast from dislocation arrays in the $\Sigma 3$, $\Sigma 29a$ and $\Sigma 43a$ related interfaces.

<table>
<thead>
<tr>
<th>DIFFRACTION VECTOR</th>
<th>$\Sigma 3$ $b=a/3[111]$</th>
<th>$\Sigma 29a$ $b=a/58[2 29 5]$</th>
<th>$\Sigma 43a$ $b=a/86[33 27 26]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm g$</td>
<td>$</td>
<td>g \cdot b</td>
<td>\</td>
</tr>
<tr>
<td>$T \ 1 \ 1$</td>
<td>M 0.33 S 0.38 S 1.0 S 1.0</td>
<td>M 0.4 S 0.62 S 0.63 S 0.77</td>
<td></td>
</tr>
<tr>
<td>$T \ 1 \ 1$</td>
<td>S 1.0 S 0.62 S 0.63 S 0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0 \ 2 \ 0$</td>
<td>M 0.67 R 0.07 0.40 S 0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0 \ 0 \ 2$</td>
<td>R 0.09 0.56 W 0.14 1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\overline{2} \ 2 \ 0$</td>
<td>R 0.02 R 0.02 0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0 \ 2 \ 2$</td>
<td>W/R 0.22 S 0.83 M/S 1.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\overline{2} \ 0 \ 2$</td>
<td>W 0.20 M/W 0.24 M/S 0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\overline{2} \ 0 \ 2$</td>
<td>W/R 1.33 W/R 0.10 0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\overline{2} \ 2 \ 0$</td>
<td>S 0.93</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S=Strong contrast, M=Medium contrast, W=Weak contrast, R=Residual contrast.
*Specimen at full tilt, low contrast from whole region.

### TABLE 6.20
Dislocation loop analysis showing the interstitial character of loops which nucleate adjacent to some grain boundaries.

<table>
<thead>
<tr>
<th>LOOP TYPE</th>
<th>INVISIBILITY OUTSIDE CONTRAST</th>
<th>HABIT PLANE</th>
<th>BURGERS VECTOR</th>
<th>LOOP NATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>220 022 $\overline{2} 20$ 020</td>
<td>$\overline{2} 20$ 020</td>
<td>$[\overline{1} 1 1]$</td>
<td>$a/3[111]$</td>
</tr>
<tr>
<td>B</td>
<td>220 $\overline{2} 02$ 220 020</td>
<td>$[\overline{1} 1 1]$</td>
<td>$a/3[111]$</td>
<td>interstitial</td>
</tr>
<tr>
<td>C</td>
<td>11$\overline{1}$ 220 1$\overline{3} 1$ 020</td>
<td>$[\overline{1} 1 1]$</td>
<td>$a/2[0\overline{1} 1]$</td>
<td>interstitial</td>
</tr>
</tbody>
</table>
7.1 INTRODUCTION

The experimental results are conveniently divided into two groups related to the role of grain boundaries in the nucleation and growth of both helium bubbles and radiation induced dislocations. In this chapter, consideration is given to the microstructural distribution of helium within grains and at grain boundaries. An analysis of the extent of bubble migration during high temperature irradiation is also given. Major emphasis is given to the nucleation density of helium bubbles at grain boundaries; the experimental results are discussed in terms of a model for bubble nucleation.

7.2 THE MICROSTRUCTURAL DISTRIBUTION OF IMPLANTED HELIUM

Implanted helium ions are stopped within the target alloy and the depth distribution is defined by Figures 5.7 and 5.8a. At high temperatures helium will diffuse rapidly to traps such as vacancies, dislocations and grain boundaries. Thus helium is effectively redistributed by diffusion. Little is known about helium mobility and trapping at various microstructural sinks. This is mainly due to the experimental limitations of TEM where bubbles down to a radius of about 1nm can be resolved. TEM cannot be used to demonstrate the presence of small (d<1nm) bubbles or helium-vacancy complexes although THDS, coupled with atomistic calculations, has demonstrated the existence of helium-vacancy clusters (section 3.2). Here, the microstructural distribution of helium is inferred from calculations of the overpressures which may arise in bubbles during implantation.
Helium bubbles nucleate and grow during high temperature implantation and are first resolvable in the TEM at grain boundaries (section 6.2.1). The density of visible bubbles within grains increases with implanted dose whereas the areal bubble density at grain boundaries remains approximately constant (section 6.2.1). After implantation at 600°C to a mean concentration of 7000appmHe only 4% of the implanted helium can be accounted for in visible bubbles (if the bubbles are assumed to be at their equilibrium size). It is necessary to account for the microstructural distribution of the remainder of the implanted helium. There are, in principle, three factors which may contribute to this apparent discrepancy:

1. Helium release during implantation.
2. Helium is present in overpressurised bubbles.
3. Helium is present in sub-microscopic vacancy clusters.

Bauer and Thomas (203) studied the re-emission of helium from 316 stainless steel during 300keV helium ion implantation in the temperature range -170°C to 700°C. They report negligible re-emission up to a dose of $10^{21}$ ions m$^{-2}$ at all temperatures, which is a factor of ten times the dose used in this work. On the basis of this evidence, it can be inferred that implanted helium remains trapped within the target material.

The two alternative explanations involve either overpressurised bubbles, where the bubbles contain more helium atoms than are strictly necessary to maintain an equilibrium pressure, or helium entrapment in submicroscopic helium clusters. Both explanations can be used to
account for some of the remaining helium and it is likely that both contribute to the apparent discrepancy. Consider the possibility of an over pressure, $P_0$, in the bubbles; if helium is assumed to behave as an ideal gas, then:

$$P_0 = \frac{3nkT}{4\pi r^2} - \frac{2Y}{r} \quad \ldots \ldots 7.1$$

The first term on the right hand side describes the pressure in a spherical bubble with radius $r$ which contains $n$ helium atoms. $k$ and $T$ are Boltzmann's constant and the absolute temperature respectively. The second term describes the equilibrium pressure where $Y$ is the surface energy. Using the data for 40keV helium ion implantation at 600°C (section 6.2.1), the bubble density is $3.0 \times 10^{21}$ m$^{-3}$ and the mean radius is $2.9 \times 10^{-9}$m. If all the helium resides in visible bubbles then each bubble contains $n$ atoms; where $n$ is the ratio of the implanted concentration to the bubble density, $n = 2.1 \times 10^5$ helium atoms per bubble. With $Y = 2$ J m$^{-2}$ (199) the overpressure, $P_0$, is calculated from equation 7.1 as $P_0 = 23$ GPa.

Such high pressures have been reported for small ($r=1$nm) helium bubbles in nickel as measured using Electron Energy Loss Spectroscopy (204) and Small-Angle X-Ray studies (205); helium was implanted at temperatures below 100°C and pressures of 30GPa (205) and 50GPa (204) were reported. The bubbles were grown at temperatures where vacancies are effectively immobile and where the bubbles grow by the mechanism of loop punching (62). In the high temperature experiments reported here, vacancies are sufficiently mobile to contribute to bubble growth so it is unlikely that such a high overpressure will develop. An estimate of the maximum bubble pressure is given by the pressure, $P$, required to cause loop-punching (section 3.3.1) where:
Here, $b$ is the magnitude of the Burgers vector of the punched loop, $b=0.25\text{nm}$; $G$ is the shear modulus, $G=77\text{GPa}$ (206). The pressure required to cause loop punching from a bubble with radius $2.9\text{nm}$ is calculated from equation 3.1 as $4\text{GPa}$, which is less than the calculated pressure in bubbles if all the implanted helium is in visible bubbles.

A more realistic estimate of the overpressure in the bubbles can be made. Cochranne (207) recently used computer simulation of TEM images to calculate the extent of the strain field associated with overpressurised bubbles and showed that the minimum overpressure required to observe strain fields was in the range $0.5\text{GPa}$ to $0.75\text{GPa}$. No such strain fields were observed in this work and it must be concluded that any overpressure in these bubbles is less than $0.5\text{GPa}$ and a significant amount of helium resides outside the resolvable bubbles.

The third explanation to account for the implanted dose is that helium is present in sub-microscopic helium-vacancy clusters. Helium atoms are strongly trapped at vacancies and up to six helium atoms can occupy a single vacancy (section 3.2); clearly if there are a sufficient number of vacancies available then a significant amount of helium may be trapped sub-microscopically. It is not strictly necessary for helium to reside in single vacancies. Trap-mutation is possible whereby the helium-vacancy complex generates an additional vacancy by emitting a self-interstitial atom (71). This process defines the early stages of bubble formation. It is quite clear from low dose implantations (section 6.2.1) that helium must reside
sub-microscopically within grains, although bubbles are resolvable at
grain boundaries. After implantation at 600°C to a dose of
7000appmHe only 4% of the implanted helium is accounted for in
equilibrium sized bubbles. If the remaining helium atoms \( (6 \times 10^{26} \text{ atoms m}^{-3}) \) reside only in He\(_6\)V complexes then \( 10^{26} \) vacancies per m\(^3\) are required to accomodate them. This vacancy concentration
is far in excess of the thermal vacancy concentration. However,
during helium-implantation each incident helium ion creates, on
average, about 60 vacancies by atomic displacements (figure 5.8a).
Some of these vacancies will be lost by recombination and by diffusion
to alternative sinks such as dislocations and the free surface but
less than 1% are required to accomodate the implanted helium atoms in
He\(_6\)V clusters. It is reasonable to conclude that some helium is
trapped sub-microscopically. If irradiation induced vacancies trap
helium atoms then, as argued by Farrell (150), implantation of helium
should be associated with an enhanced growth of interstitial
dislocation loops because more self-interstitial atoms survive
recombination. Such an observation was reported in section 6.2.2 and
lends tentative support to the proposed entrapment of helium in
radiation induced vacancies. Similar observations of enhanced
dislocation formation in the presence of helium was reported in
stainless steel (208) and in Nimonic PE16 alloy (34). Shaw et al (34)
proposed an alternative explanation; helium trapped at dislocations
could modify the interaction of interstitials with growing dislocation
loops, allowing interstitials to cluster more readily. The trapping
of helium at dislocations could account for some of the implanted
helium where the elastic interaction between a helium atom and a
dislocation could result in helium entrapment (section 2.2).
However, the dislocation density is not considered sufficient to trap
A major problem is identified here, since TEM can only be used to resolve bubbles down to a diameter of 1 nm, it is not possible to gain direct evidence for the nucleation of helium bubbles. Thus, the factors which control the growth of sub-microscopic helium-vacancy clusters into resolvable bubbles cannot easily be determined. Visible bubbles were distributed heterogeneously within grains, for example at interstitial dislocation loops and in the vicinity of dislocations, but few bubbles decorated dislocation lines (figure 6.2). Presumably, the distribution of sub-microscopic clusters (bubble nuclei) is homogeneous; it may be that bubble growth is enhanced due to differential fluxes of vacancies and interstitials in the vicinity of dislocations but this problem remains unsolved. Farrell and Packan report heterogeneous cavity distributions in a dual-beam irradiated model austenitic alloy (167). The heterogeneity took the form of short rows, sheets and clouds of cavities. It was argued that nucleation occurred at clusters of impurity atoms, possibly oxygen, that were previously associated with dislocations during earlier thermo-mechanical treatment. It may be that similar heterogeneities exist in this work, the lines of bubbles in figure 6.2a and 6.2b are not aligned along the visible dislocations.

The density of bubbles within grains was sensitive to the helium/dpa ratio during dual-beam irradiation (section 6.2.1). Due to the uncertainty of the implanted doses when using two ion beams it is unrealistic to make a quantitative analysis of the results. However, it is clear that the percentage of the implanted helium in visible bubbles is enhanced during dual-beam irradiation and may be attributed...
to the release of helium from sub-microscopic traps. Hall and Wiedersich used a rate theory approach to determine the dominant detrapping mechanism for helium during irradiation at high temperatures (56). Three mechanisms were considered for the detrapping of helium from vacancies; thermal release, radiation resolution and self-interstitial replacement. Calculations showed that the radiation induced interstitial concentration was so high that interstitial replacement was the dominant detrapping mechanism at all temperatures up to 800°C. Considering the dual-beam experiments here, it is likely that the same detrapping mechanism dominates because self-interstitials are not only created by displacement events but also by the implantation of chromium-ions themselves. The enhanced bubble volume after dual-beam irradiation is consistent with an enhanced rate of helium detrapping, thereby releasing mobile helium which contributes to the growth of helium bubbles.

7.2.2 THE DISTRIBUTION OF HELIUM AT GRAIN BOUNDARIES.

In contrast to the observations of gas bubble formation within grains, the density of bubbles at grain boundaries does not vary with dose (section 6.3.2.2). Bubbles are observed at grain boundaries before any are resolved within grains. Some of the implanted helium within grains is present in sub-microscopic helium-vacancy clusters and as the dose is increased, more bubbles become resolvable in the TEM. Since the density of bubbles at grain boundaries does not vary with dose it is unlikely that a growing population of sub-microscopic helium-vacancy clusters exists at grain boundaries.

Zones, denuded of bubbles were identified adjacent to grain
boundaries after implantation at 600°C (section 6.3.1). The denuded zones were symmetrical about the boundary position and were 100nm wide in total. It was not possible to define bubble denuded zones after implantation to low doses because few bubbles were resolvable within grains. The symmetrical nature of the bubble denuded zones indicates that they are not a result of boundary migration during implantation and it can be inferred that the bubbles observed at grain boundaries are a result of preferential bubble nucleation and not of bubble sweeping by migrating boundaries. The concentration of helium at grain boundaries was estimated in section 6.3.3. The helium concentration is approximately the same at all grain boundaries, despite the boundary to boundary variation of both bubble size and bubble density. Furthermore, if the bubbles are assumed to be at their equilibrium size, the concentration of helium at grain boundaries corresponds to a capture volume which is only about 20nm wide at 600°C (table 6.12). This capture volume was independent of dose, dose rate and dual beam irradiation but increased with temperature, which is consistent with helium diffusing from a narrow vacancy free band to the grain boundaries. As long as there is a positive binding energy for helium atoms at grain boundaries the concentration of helium should not vary from interface to interface.

The width of the helium capture volume associated with grain boundaries is only 20% of the width of the denuded zone (as measured at 600°C). The size of the denuded zone was defined in figure 6.15. However, some bubbles did nucleate and grow within the 50nm wide zone; some of the implanted helium can be accounted for in these bubbles. It becomes necessary to consider the origin of the bubble denuded zone. Bubble denuded zones can, in principle, develop due to
either (or both) vacancy loss or helium loss to the interface. Vacancy adsorption at grain boundaries is well known and results in void denuded zones as discussed in section 4.3. Helium bubble denuded zones have been reported (see Table 3.3) but bubble distributions frequently extend right up to the interface suggesting little or no helium denudation. The width of a denuded zone is determined by the diffusivity of the denuded species (209); in the absence of vacancies helium will diffuse rapidly as an interstitial atom. But helium is effectively trapped in vacancies and the effective diffusion coefficient is determined by the detrapping rate and the vacancy concentration (39). Consider figure 7.1 in which the vacancy concentration is shown schematically as a function of distance from a grain boundary. The effective diffusion coefficient will be determined by the vacancy concentration (39); when the vacancy concentration is high the diffusion coefficient is low because detrapped helium atoms only diffuse short distances between vacancies (region B). The detrapping rate will be controlled by thermal release in the absence of irradiation (39) but during irradiation helium detrapping is most likely to occur by self-interstitial replacement (56). Nearer to the interface (region A, figure 7.1) the vacancy concentration is low; the distance travelled by a migrating interstitial atom between vacancies is much greater. Thus, the effective diffusion coefficient of helium is higher in the immediate vicinity of grain boundaries. The result of this model for helium mobility is that significant amounts of helium may be trapped within the vacancy denuded zone but close to the interface implanted helium atoms retain mobility and reach the boundary. Green et al (118) invoke a similar argument to explain their observations of bubble formation in 600MeV proton irradiated aluminium. They proposed that
trapped helium is present within the vacancy denuded region adjacent to grain boundaries.

The observation of a 100nm wide bubble denuded zone in this work is consistent with vacancy denudation but is in direct contrast to the observations of Bennetch et al (115). They implanted 80keV helium-ions into annealed 316 stainless steel in the temperature range 500°C to 650°C. The implantations were carried out in-situ in the TEM; bubbles were resolvable at grain boundaries before any could be resolved within grains. But at higher doses, bubbles were observed within grains and there was little or no denudation at grain boundaries. Similarly, Farrell and Packan (114) observed a high density of small bubbles within the grains of Nimonic PE16 alloy after triple beam irradiation at 600 °C. The bubbles extended up to the grain interfaces where there was a bubble free zone only 15nm wide.

It is apparent from these observations that helium does not diffuse over large distances within austenitic grains but is effectively trapped in small gas bubbles. It is not clear what factors determine the formation of bubble denuded zones since these may or may not form in apparently similar experiments.

The general conclusion from the above discussion is that the bubble denuded zone is associated with vacancy denudation where there are insufficient vacancies for bubbles to grow to resolvable sizes; helium is trapped in sub-microscopic clusters within these regions. An alternative interpretation is that all the helium which is implanted into the 100nm wide bubble free zone is sufficiently mobile to reach the grain boundary. If this is the case then the bubbles at grain boundaries must contain approximately five times more helium.
than is necessary to maintain an equilibrium pressure. For bubbles with radius 2.6nm and an areal density of $1.4 \times 10^{15} \text{ m}^{-2}$ (Table 6.11) this corresponds to an overpressure of 5.8GPa (calculated using equation 7.1). As previously discussed, such high overpressures are sufficient to generate visible strain fields in the electron microscope and are high enough to allow growth by loop punching. No strain fields were observed and, furthermore, bubbles at grain boundaries are unlikely to develop such high overpressures. Consider an overpressurised bubble at a grain boundary. The pressure in the bubble can be relieved either by absorbing a vacancy or by emitting an interstitial atom. A grain boundary can act as a vacancy source (154) and the overpressure in a bubble may be sufficient to generate vacancies locally. Alternatively, the bubble may emit interstitial atoms which are then plated out elsewhere in the interface in a similar way to interstitial emission during loop punching (62). Interstitial atom emission is easily accommodated at a grain boundary compared to that within grains so single interstitials may be emitted. The process at grain boundaries will be driven by lower overpressures. Hence, bubbles at grain boundaries cannot develop high overpressures although some overpressure is possible. On this basis, it must be concluded that the capture volume for helium atoms at grain boundaries is smaller than the total width of the observed bubble denuded zone.

7.3 MIGRATION OF HELIUM BUBBLES DURING IMPLANTATION

The observed distribution of helium bubbles was highly heterogeneous. The bubbles were associated with grain boundaries, grain boundary dislocations and with faulted dislocation loops within grains. Previous workers have proposed preferential bubble nucleation
at matrix dislocations (123), at grain boundaries and at grain boundary dislocations (100,105). However, these observations were made after long annealing periods following low temperature implantation. It is not clear from such results that bubbles nucleate heterogeneously because both dislocation motion and bubble migration are possible during long annealing periods. In the present work, implantations were performed at high temperatures and in short periods of time (typically less than 20 minutes) where bubble migration is limited. To confirm that bubbles nucleate preferentially it is necessary to demonstrate that bubble migration effects are minimal. The migration rate of bubbles is considered and it will be shown that migration distances are small and that the observed distributions reflect the nucleation characteristics of helium bubbles.

Random migration of helium bubbles can in principle occur by a variety of mechanisms (section 3.2.2) and there is conflicting evidence for the mechanism which operates in stainless steels. Volume diffusion, surface diffusion and vapour transport have all been reported as the controlling mechanism for bubble motion. Surface diffusion controlled migration is likely to be the fastest migration mechanism (80) so use of an appropriate surface diffusion coefficient, $D_s$, will lead to an upper limit to the diffusion coefficient of a bubble, $D_b$. In the absence of any data for $D_s$ in stainless steels a value is extrapolated from the data of Smidt and Pieper (83). In their experiments, surface diffusion coefficients were calculated from the growth rate of helium bubbles in 316 stainless steel during high temperature annealing between 800°C and 1100°C. Surface diffusion controlled growth was inferred and the bubble diffusion coefficient, $D_b$, was related to the surface diffusion coefficient,
where \( a \) is the lattice parameter and \( r \) the bubble radius. By extrapolation of the data to 600°C the surface diffusion coefficient is given as \( 10^{-20}\text{m}^2\text{s}^{-1} \) with an upper limit (due to experimental scatter) of approximately \( 10^{-18}\text{m}^2\text{s}^{-1} \).

Since an estimate of the maximum likely distance travelled by a migrating bubble during high temperature irradiation is required then a value of \( D = 10^{-18}\text{m}^2\text{s}^{-1} \) is assumed. This diffusion coefficient is much lower than the expected value (e.g. \( 10^{-13}\text{m}^2\text{s}^{-1} \) for pure nickel) (210). A similar discrepancy of the order of \( 10^3 \) to \( 10^5 \) was reported by Smidt and Pieper from bubble size measurements in vanadium (211). A possible explanation of this discrepancy is due to Greenwood who argued that relationships relating \( D_s \) to \( D_b \) (such as equation 7.2) are an over simplification (107). During random bubble migration any atom movement on the surface will locally alter the curvature, with the result that there is a high probability that the subsequent jump will return the bubble to its original position. This correlation effect means that only a small proportion of atom jumps contribute to bubble migration and that \( D_s \) measured from bubble migration experiments are only an effective surface diffusion coefficient.

The diffusion coefficient of a bubble with radius 1nm is calculated as \( D_b = 1.2 \times 10^{-21}\text{m}^2\text{s}^{-1} \) from equation 7.2.

The three dimensional mean square distance, \( x \), travelled by a bubble in time, \( t \), is given by:

\[
x = \sqrt{6D_b t}
\]

During the irradiation period (typically 1200s) the distance travelled
by a 1nm radius bubble is only 3nm. This estimate represents the furthest distance that a bubble will travel since it is based on the fastest migration mechanism; if other migration mechanisms operate then bubbles will migrate over even smaller distances. Clearly, both bubbles at grain boundaries and bubble denuded zones cannot be a result of bubble migration. Similarly, the observation of bubbles at faulted dislocation loops and in strings is the result of heterogeneous bubble nucleation rather than homogeneous nucleation because bubbles cannot migrate over the large distances required to create the observed bubble distributions.

The bubble density at grain boundaries was shown to be a function of gas implantation rate and temperature and was enhanced by GBDs at the interface. Since bubbles are effectively pinned at the interface (section 3.4.1) migration is limited to the boundary plane. In these experiments, bubble migration is limited to small distances but the coalescence rate of bubbles at grain boundaries is enhanced relative to that within grains due to the limit of two dimensional migration in the boundary. Wolfenden and Farrell (106) give the coalescence time of bubbles within the boundary plane as:

\[ t_c = \frac{1^4}{32r^2D_b} \]  

In these experiments, the inter-bubble spacing \( l \) is typically \( 1.7 \times 10^{-8} \text{m} \) (density=\( 10^{15} \text{m}^{-2} \)) and for 1nm radius bubbles the diffusion coefficient (for surface diffusion controlled migration) is \( D_b=1.2 \times 10^{-21} \text{m}^2\text{s}^{-1} \). The coalescence time given by equation 3.2 is \( t_c=2 \times 10^6 \text{s} \). In this study the irradiation times are of the order of \( 10^2 \text{s} \). It is clear that the observed bubble densities reflect the nucleation density since bubble coalescence is unlikely.
Helium bubble migration may be directed due to the interaction of a bubble with the strain field of a dislocation (section 3.4.2). The observation of bubble alignment at grain boundary dislocations could be attributed to bubble migration rather than to preferential nucleation. Weeks et al (125) derived an expression for the volume of radius \( R^* \) from which all bubbles should be drawn onto a straight screw dislocation in time \( t \) (assuming surface diffusion controlled migration):

\[
R^* = \left[ \frac{20 D_s \Omega^2 G (1-v) t}{\pi^2 kT r (7-5v)} \right]^{1/4} \quad \ldots \ldots 3.3
\]

The terms in equation 3.3 are described in section 3.4.2. For austenitic stainless steel Poisson's Ratio, \( v = 0.285 \) and the shear modulus, \( G = 77 \text{GPa} \) (206). For migration at 600°C and using \( D_s = 10^{-18} \text{m}^2\text{s}^{-1} \) (extrapolated from the data of Smidt and Pieper (83)) \( t = 1200 \text{s} \) and \( \Omega = 8.2 \times 10^{-30} \text{m}^3 \), \( r = 1 \text{nm} \), all bubbles within a radius of \( R^* = 3.3 \text{nm} \) should be drawn onto a screw dislocation. To a first approximation this calculation can be applied to grain boundary dislocations but GBDs generally have smaller Burgers vectors (and hence smaller strain fields) than lattice dislocations and are not perfect screw in character. The calculation does not rule out the possibility of bubble migration onto GBDs, particularly when the dislocation spacing is small. However, if bubble migration onto dislocations is the only mechanism for alignment along GBDs then not all bubbles will be aligned, particularly at dislocation spacings greater than \( 2R^* = 7 \text{nm} \). The observation of bubbles aligned along GBDs at lower irradiation temperatures (as low as 450°C) lends further support to the case for preferential nucleation since, during these irradiations, bubble mobility will be lower. A mechanism for preferential nucleation of helium bubbles at GBDs is discussed later.
The density of helium bubbles at grain boundaries is an important parameter in a variety of models describing high temperature helium embrittlement (24-28). Despite the demand for a solution to the embrittlement problem our understanding of the nucleation of helium bubbles at grain boundaries is poor. Evidence for the factors which control the bubble nucleation density at grain boundaries is limited (section 3.4.1). In this section, the characteristics of gas bubble formation at grain boundaries are discussed with reference to a model describing the nucleation density of helium bubbles at grain boundaries.

Coherent twin interfaces were the only boundaries which did not exhibit preferential bubble nucleation, presumably because there is little or no binding interaction between helium atoms and the interface. The possibility of a helium-twin interaction is discussed in a later section (section 8.1.2). All other crystal interfaces, including the various facets of a low angle grain boundary (Figures 6.24 and 6.26) exhibit preferential bubble nucleation. The areal density of bubbles at grain boundaries increased as a function of implantation rate (section 6.3.2.2), showed a weak dependence on implantation temperature (section 6.3.2.1) but was independent of extra displacement damage during dual-beam irradiation (section 6.3.2.3). The presence of resolvable GBDs at interfaces enhanced the nucleation density of helium bubbles at all irradiation temperatures studied. Bubbles decorated the GBDs when the GBD spacing was sufficiently large to resolve the alignment.
A model was developed for the nucleation of helium bubbles at grain boundaries and at GBDs and can be used to explain the experimental observations made in section 6.3. The model is based on the three dimensional analysis of Greenwood et al. (62) for the homogeneous nucleation of fission gas bubbles within the grains of fissile material. In the present analysis the model is modified to account for both two dimensional diffusion in the boundary plane and one dimensional diffusion along the cores of interfacial dislocations. The model is described qualitatively as follows; implanted helium atoms will diffuse rapidly, by an interstitial mechanism, until they become trapped at a lattice defect or a grain boundary. Those helium atoms which are implanted in the vicinity of the interface within the vacancy denuded zone will eventually encounter the interface to which they will become bound (since helium is virtually insoluble in the matrix). The helium atoms are free to diffuse in two dimensions within the boundary plane until they encounter other helium atoms. Two helium atoms are considered to form a stable bubble nucleus. Helium bubbles are nucleated until a newly arrived helium atom is more likely to reach an existing nucleus than another single gas atom. When dislocations are present at the interface they act as additional trapping sites and helium atoms are only able to diffuse in the boundary plane until they become trapped at the dislocation cores. Then diffusion is limited to one dimension along the dislocation core. Again bubble nucleation is assumed to take place when two helium atoms meet.
Steady-state diffusion conditions are assumed to exist between a bubble nucleus and the surrounding region of interface; thereby the steady-state diffusion equation can be used. This approximation applies except in the very early stages of irradiation where the interface is essentially occupied with single gas atoms. In the case of two dimensional diffusion it is further assumed that the boundary diffusion coefficient of helium is isotropic. Following the analysis of Greenwood et al (62), negligible solubility of helium is assumed. It is not clear that this assumption is valid; indeed, Greenwood (107) recently suggested that there may be a finite solubility of helium at grain boundaries. There is no experimental evidence which supports this proposal. Baskes and Vitek (42) recently used atomistic computer calculations to show that there is a large dilatational field around a helium atom at a grain boundary, i.e. there is a large strain energy associated with a helium atom. Thus, the solubility of helium at grain boundaries is likely to be low. Also following the analysis of Greenwood et al (62), a di-helium complex is assumed to form a stable bubble nucleus, which is in agreement with other recent models for helium bubble nucleation within grains (65,66). Ghoniem and Takata (42) argue that a di-helium cluster is not stable against thermal dissociation or radiation resolution. A tri-helium complex was assumed to form the critical bubble nucleus; their model was appropriate to neutron irradiation at high temperatures where the radiation times are long, allowing for some time dependent thermal dissociation and where the helium/dpa ratio is low relative to the experiments reported here. During the short irradiation periods and with a high helium/dpa ratio the effects of thermal dissociation and radiation resolution are considered negligible.
The derivation of the model for bubble nucleation is based on the assumptions outlined above. Consider the two dimensional case first. Let $G_B$ be the rate of arrival of helium atoms at a grain boundary (in units of gas atoms per atom site per second). If $D_B$ is the gas atom diffusion coefficient in the boundary and $C$ the atomic concentration of helium at the interface, the steady state diffusion equation is:

$$D_B \nabla^2 C = -G_B$$

Let the radius of a bubble nucleus be $r_o$ and let $r_2$ be the radius of the approximately circular catchment area of the interface surrounding each nucleus so that the spacing of bubble nuclei is about $2r_2$. For two dimensional diffusion we have:

$$\nabla^2 C = -\frac{G_B}{D_B} \left( \frac{\partial^2 C}{\partial r^2} \right) + \frac{1}{r} \left( \frac{\partial C}{\partial r} \right)$$

......7.3

Given the boundary conditions $\partial C / \partial r = 0$ when $r = r_2$ and $C = 0$ when $r = r_0$ (i.e. assuming that there is negligible helium solubility in the interface) we find by integration of equation 7.3:

$$r \frac{\partial C}{\partial r} = -G_B r^2 + K$$

Where $K$ is a constant. Given the first boundary condition we have:

$$\frac{\partial C}{\partial r} = -\frac{G_B}{2D_B} \left( \frac{r^2 - r_o^2}{4} \right)$$

Further integration and inclusion of the second boundary condition yields:

$$C = \frac{G_B}{4D_B} \left( r_o^2 - r^2 + 2r^2 \log_2 \left( \frac{r_2}{r_o} \right) \right)$$

......7.4

If $r_2 >> r_o$ then:

$$C_2 = C(r_2) = \frac{G_B r_2^2}{4D_B} \left( 2 \log_2 \left( \frac{r_2}{r_o} \right) - 1 \right)$$

......7.5
This is the concentration of gas atoms in the interface at points midway between the nuclei and is (to a first approximation) the mean gas concentration at the interface. If \( v \) is the jump frequency of gas atoms at the interface and \( a \) is the jump distance then:

\[
v = 4D_B \frac{a}{a^2}
\]

Where the number of possible jumps from a particular site in the interface is approximately four. Let the lifetime of a gas atom at the interface before reaching the nucleus be \( T \), then:

\[
T = \frac{n}{v}
\]

Where \( n \) is the number of jumps made per atom lifetime. Since \( C_2 = G_B T \), then:

\[
n = \frac{vC_2}{G_B a^2} = \frac{r_2^2}{2\log_e(r_2/r_0) - 1}
\]

The homogeneous nucleation separation is now derived by assuming that the number of bubble nuclei increases until there are so many that a newly created gas atom is more likely to reach an existing nucleus than meet another gas atom. The average number of jumps made by a gas atom before it meets another is:

\[
n_g = \frac{1}{zc_2}
\]

Where \( z \) is the number of new sites explored per jump (about 2). So:

\[
n_g = \frac{2D_B}{G_B r_2^2[2\log_e(r_2/r_0) - 1]}
\]

Existing nuclei are likely to be reached if \( n_g > n \), that is from 7.6 and 7.7, if:

\[
\frac{2D_B}{G_B r_2^2[2\log_e(r_2/r_0) - 1]} > \frac{r_2^2}{a^2} [2\log_e(r_2/r_0) - 1]
\]
The homogeneous nucleation separation is therefore given by $2r_2$, where:

$$r_2 = \frac{[2D_D a^2]^{1/4}}{[G_B]^{1/4} \left[2 \log_e (r_2/r_0) - 1 \right]^{1/2}}$$

Note that $r_2$ occurs on both sides of equation 7.8, which must be solved numerically.

A similar analysis was used for bubble nucleation at grain boundary dislocations assuming one dimensional gas atom diffusion along the dislocation cores. The one-dimensional steady state diffusion equation is simply:

$$\frac{\partial C}{\partial r^2} = \frac{D_D}{\partial r^2}$$

Where $D_D$ is the gas atom diffusion coefficient along the dislocation line. Let the radius of a bubble nucleus be $r_0$ and let $r_1$ be the spacing of nuclei along the dislocation line. The solution of equation 7.9 which satisfies the boundary conditions $C=0$ when $r=r_0$ and $\partial C/\partial r=0$ when $r=r_1$ is:

$$C = \frac{G_D}{D_D^2} \left[2r_1(r-r_0)+(r_0^2+r^2)\right]$$

If $r_1 >> r_0$, then:

$$C(r_1) = \frac{G_D r_1^2}{2 D_D}$$

This is the concentration of gas atoms along the dislocation line at points midway between bubble nuclei and is approximately the mean helium concentration along the dislocation. Following the same arguments as for two dimensional diffusion (but with modified approximations) the jump frequency of gas atoms along the dislocation line is given by:

$$v = \frac{2D_D}{a^2}$$

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Where the number of possible jumps from a particular site is only 2 for one-dimensional diffusion. Since only one new site is explored per jump, the number of jumps made by a gas atom before reaching a nucleus is:

$$n = \frac{r^2}{a^2}$$

The number of jumps made before reaching another gas atom is thus:

$$n_g = \frac{2D_D}{G_D r_1^2}$$

Existing nuclei will be reached if $n_g > n$ and the nucleus separation, $2r_1$, is given by:

$$r_1 = \left[ \frac{2D_D a^2}{G_D} \right]^{1/4} \quad \text{......7.11}$$

If equations 7.8 and 7.11 are to be useful it is necessary to make realistic estimates of the gas atom arrival rates $G_B$ and $G_D$ and of the helium diffusion coefficients $D_B$ and $D_D$. To establish the gas atom arrival rate at grain boundaries, $G_B$, it is assumed that all bubbles visible at the interface are at their equilibrium pressure and that the gas obeys the ideal gas law. This may underestimate the gas atom arrival rate since the bubbles may contain an overpressure (section 7.2.2) but the fourth root must be taken of any factor which is introduced to account for the overpressure (equation 7.8) so any large deviations from the calculated bubble spacings are precluded. The assumption is consistent with the observed dependence of bubble size on bubble density at grain boundaries (section 6.3.3). From that analysis it was shown that, assuming equilibrium sized bubbles, the helium capture volume at grain boundaries was approximately 19.5nm wide for all implantations at 600°C. This is the capture volume used in this
analysis for all implantations at 600°C. The capture volume increased with implantation temperature (Table 6.12); the temperature dependence of the gas atom arrival rate \( (G_B) \) is discussed in the following analysis. In calculating \( G_B \) in units of atoms per atom per second it was assumed that the boundary consists of a single layer of close packed atoms \( (1.8 \times 10^{18} \text{m}^{-2}) \).

If the interface contains discrete grain boundary dislocations (GBDs) then the arrival rate of helium atoms at a GBD, \( G_B \), depends on the dislocation spacing, \( d \). The two cases which need to be considered are illustrated in Figure 7.2. If \( d \) is larger than twice the two-dimensional bubble nucleation spacing \( r_2 \) then each GBD will be decorated with bubbles at a spacing \( 2r_1 \) and will have a double denuded zone of full width \( 2r_2 \). Between the dislocations there will be a bubble population of spacing \( r_2 \) (Figure 7.2a). If \( d < 2r_2 \) then bubble nucleation between GBDs is inhibited and bubbles will be attached to GBDs at an average spacing (along the GBD) of \( 2r_1 \) (Figure 7.2b). Since the catchment area from which each GBD can collect gas is limited either by \( r_2 \) (case a) or \( d \) (case b) the variation of \( G_B \) with \( d \) is:

\[
G_B = \frac{G_B 2r_2}{a} \quad \text{(case a)}
\]

or

\[
G_B = \frac{G_B d}{a} \quad \text{(case b)}
\]

Where the factor \( a \) is introduced to keep all \( G \) parameters in units of atoms per atom per second. Equation 7.11 can now be expanded to:

\[
r_1 = \left[ \frac{2D_B a^3}{G_B d} \right]^{1/4} \quad \text{(case b)}
\]

Thus, for case b \( (d < 2r_2) \), the total bubble nucleation density, \( \rho_1 \), in the presence of GBDs is given by:
The bubble density in the absence of GBDs is simply:

\[ \rho_2 = (2\sqrt{3} r_2^2)^{-1} \quad \text{(7.13)} \]

assuming close packing of the circular regions around bubble nuclei.

Two expressions have been derived relating the bubble nucleation density at grain boundaries to the diffusion coefficients \( D_B \) and \( D_D \), and the gas atom arrival rate \( G_B \), and, in the case of nucleation at GBDs, \( d \) the dislocation spacing. Estimation of the diffusion coefficients \( D_B \) and \( D_D \) for helium at grain boundaries and along GBDs is difficult because the diffusion of helium in metals is poorly understood. Little is known about the grain boundary diffusion coefficient of small interstitial atoms (42). De Hosson et al (37) used atomistic computer calculations to show that the migration energy of interstitial helium atoms along perfect, straight edge dislocations did not differ appreciably from that in the bulk. However, the presence of jogs along dislocations may inhibit migration (section 2.2). In the absence of any experimental data the nucleation model has been used to show consistency between experimental data and model predictions with assumed values of \( D_B \) and \( D_D \).
7.4.2 THE ROLE OF GAS IMPLANTATION RATE

The bubble density at grain boundaries increases as a function of gas implantation rate (section 6.3.2.2). In terms of the bubble nucleation model an increase in the gas implantation rate results in an increased gas arrival rate at the interface and, from equations 7.8 and 7.13 an increase in the bubble density should be expected. Qualitatively, the nucleation model successfully describes the observed trend. Figure 7.3 shows the measured bubble density as a function of the gas implantation rate at 600°C for the data tabulated in tables 6.6 (column 3), 6.8, 6.9 and 6.10. Boundaries which exhibit a visible dislocation structure are not included. Data from both single beam helium implantations (70keV and 40keV) to various doses and from dual beam irradiations are included. The error band represents the error in the determination of bubble density due to the approximation of constant foil thickness (calculated error due to thickness variation of 150nm+/-50nm and projected boundary width of 130nm, bubble density of 1x10^{15}m^{-2}). Although the error due to the thickness assumption may be as high as +/-20\% it is clear that the observed experimental scatter of +/-60\% of the mean cannot be accounted for by errors due to the thickness approximation alone. The additional scatter in the results represents a true boundary to boundary variation in bubble density. Figure 7.3 shows a clear trend to higher bubble densities with increased implantation rate and the effect is independent of dose, helium-ion beam energy and dual beam irradiation.

The full lines in Figure 7.3 show the increase in bubble density with gas implantation rate predicted by the nucleation model (equation
assuming a variety of diffusion coefficients for helium at grain boundaries. The predicted trend shows good agreement with the experimental data points; the majority of points correspond to a diffusion coefficient within the range $1 \times 10^{-14}$ to $1 \times 10^{-13}$ m$^2$s$^{-1}$ with $2 \times 10^{-14}$ m$^2$s$^{-1}$ as a typical value. The range of bubble densities for each implantation rate can, therefore, be explained by a boundary dependent diffusion coefficient for helium although anisotropy in the boundary diffusion coefficient may contribute to some scatter; the nucleation model assumes an isotropic (radial symmetry) boundary diffusion coefficient. Anisotropy of boundary diffusion will impose directional constraints on the nucleation process.

Consider the diffusion coefficient for helium at grain boundaries predicted in this analysis, $D = 2 \times 10^{-14}$ m$^2$s$^{-1}$. This may be compared with a fast interstitial migration mechanism within grains or with grain boundary self- and impurity-diffusion. The diffusion coefficient for interstitial helium atoms in stainless steel may be estimated from the equation (67):

$$D_I = 2 \times 10^{-8} \exp(-0.25eV/kT) \text{ m}^2\text{s}^{-1} \quad \ldots \ldots 7.14$$

The boundary self-diffusion coefficient was determined experimentally in the temperature range 590$^\circ$C to 900$^\circ$C for an Fe, 19.9%Cr, 24.7%Ni alloy (213) where:

$$D_B = 1.66 \times 10^{-3} \exp(-1.9eV/kT) \text{ m}^2\text{s}^{-1} \quad \ldots \ldots 7.15$$

A second, general expression for grain boundary self- and impurity diffusion is given by (213):

$$D_B = 10^{-4} \exp(-9.35T_m/kT) \text{ m}^2\text{s}^{-1} \quad \ldots \ldots 7.16$$
Here, $T_m$ is the absolute melting point of the metal (approximately 1700K for austenitic alloys(12)). The expression is a generalised description of the grain boundary diffusion coefficient in a wide variety of systems and is appropriate to the temperature range $T_m / T < 2.4$ ($600^\circ$C is equivalent to $T_m / T = 2.0$). The diffusion coefficients given by equations 7.14, 7.15 and 7.16 at $600^\circ$C are $7.2 \times 10^{-10}$, $1.7 \times 10^{-14}$ and $7.6 \times 10^{-13} \text{m}^2\text{s}^{-1}$ respectively. The diffusion rate for helium at grain boundaries is given by the nucleation model as $2 \times 10^{-14} \text{m}^2\text{s}^{-1}$ and is similar to the rate of grain boundary self-diffusion given by equation 7.15 and is significantly slower than the rate of helium-interstitial migration within grains. Grain boundary self- and impurity-diffusion are generally thought to occur by a vacancy type mechanism (42); the bubble nucleation model as applied to the experimental results is consistent with helium diffusing by a vacancy mechanism at grain boundaries. This conclusion is supported by three recent studies. Philipp, Sonnenberg and Williams (49) measured the release of helium from implanted nickel and stainless steel specimens at high temperatures ($<1023\text{K}$). The same diffusion coefficient was reported in both polycrystalline and single crystal specimens. The implication is that grain boundaries are not a fast diffusion path relative to diffusion through the grains; diffusion within grains was consistent with 'hindered' interstitial migration between thermal vacancies. Balluffi (40) recently reviewed the results of a dynamic computer calculation to study diffusional jump processes at a high angle grain boundary. He found that self-interstitial atoms are strongly bound at local trapping sites in the boundary and are rendered immobile. Self-interstitials would not be expected to contribute significantly to boundary self-diffusion rates which is consistent with the general
conclusion that grain boundary diffusion occurs by a vacancy mechanism (40). Baskes and Vitek (42) recently calculated that helium atoms, although smaller than self-interstitials, behave like interstitial atoms in certain special boundaries, i.e., there is a strong dilatational field around a helium atom. The conclusion is that helium atoms, like self-interstitials, are strongly bound at local sites in a grain boundary and only diffuse as rapidly as a vacancy mechanism will allow.

An important feature of figure 7.3 is that the bubble density at grain boundaries is independent of both dose and He/dpa ratio (during dual-beam irradiation). The insensitivity to dose is consistent with the nucleation model where the nucleation stage is complete when the boundary is occupied by di-helium complexes at a density defined by the homogeneous nucleation spacing \(2r_2\). Thus the nucleation of bubbles at grain boundaries is complete at a sub-microscopic level; the only observable effect of dose is an increase in bubble size which is consistent with the growth of a fixed number of helium bubbles.

Both the size and density of helium bubbles at grain boundaries remain unchanged by additional displacement damage during dual beam irradiation. In marked contrast, the density of bubbles within grains is enhanced significantly by additional displacement damage. In terms of the bubble nucleation model the bubble density at grain boundaries is effectively controlled by the gas atom arrival rate, \(G_B\), and by the diffusion coefficient of helium at grain boundaries, \(D_B\) (equation 7.8). The nucleation density remains unaffected by the helium/dpa ratio which implies that both \(G_B\) and \(D_B\) are independent of the displacement rate. The helium atoms which reach
the grain boundaries are those which are implanted adjacent to the interface within the point defect denuded zone. The gas atom arrival rate at the interface may, in principle, be controlled by either the gas implantation rate or the diffusion rate of helium within the denuded zone since either process may be rate controlling. The migration rate of helium is effectively controlled by the concentration of vacancies which act to trap the gas atoms (section 2.3), however, since the atoms are implanted into a vacancy denuded zone a fast interstitial diffusion mechanism will operate at least in the immediate vicinity of the interface where the vacancy concentration is low (figure 7.1). The implication is that the gas implantation rate, rather than the migration rate of helium atoms to the interface, controls the arrival rate of helium atoms at the grain boundary. This is consistent with the experimental results since the capture volume for helium at a grain boundary is insensitive to irradiation condition.

The other factor which controls the nucleation density of bubbles at grain boundaries is the gas atom diffusion coefficient, $G_B$. The migration behaviour of helium in metals is complex and is a function of the radiation environment (43). The detrapping rate of helium from lattice vacancies determines the effective diffusion coefficient within grains and the detrapping rate may, in principle, be controlled by thermal release, by radiation induced detrapping or by self-interstitial replacement (56). As discussed earlier (section 7.2.1), a self-interstitial replacement mechanism is likely to dominate the detrapping of helium from vacancies during dual-beam irradiation. It is not clear that a similar detrapping mechanism will enhance the diffusion of helium at grain boundaries. Detrapping
enhances the mobility of helium within grains because interstitial helium atoms are highly mobile and trapping sites (vacancies) are widely spaced so that diffusing helium atoms migrate over significant distances between traps. At grain boundaries, helium atoms behave as interstitials (42) which are effectively immobile in the interface (40). A detrapped helium atom at a grain boundary will thus migrate slowly to the next trapping site. Thus, rapid diffusion is impaired and irradiation does not significantly enhance the migration rate of helium atoms at grain boundaries. It is concluded that the diffusion coefficient of helium at grain boundaries is controlled by a vacancy mechanism and the processes which control the mobility of helium atoms within grains are ineffective at grain boundaries.

The nucleation density of bubbles at grain boundaries has been measured over a relatively narrow range of gas implantation rates. In principle, the model for helium bubble nucleation may be applied to neutron irradiation where the gas generation rates are much lower than those during ion-implantation. It is necessary to estimate the gas atom arrival rate at grain boundaries. If the capture volume associated with a grain boundary is independent of the irradiation conditions (except for temperature) then \( G_B \) can be estimated from the volume gas atom generation rates by assuming a capture width of 20nm (section 6.3.1). The helium generation rates due to neutron irradiation in experimental fission reactors are \( 5 \times 10^{-7} \) appmHe\(^{-1} \) for EBR-II and \( 5 \times 10^{-5} \) appmHe\(^{-1} \) for HFIR (6) and the gas atom arrival rates at grain boundaries are estimated as \( 2.5 \times 10^{-10} \) helium atoms/atom s\(^{-1} \) and \( 2.5 \times 10^{-8} \) helium atoms/atom s\(^{-1} \) respectively. At 600°C, the diffusion coefficient for helium at grain boundaries (equation 7.8) is
2x10^{-14} \text{m}^2 \text{s}^{-1} \text{ from figure 7.3} \) and the interbubble spacing, \( 2r_2 \), is calculated as approximately 900nm for EBR-II irradiation and about 320nm for neutron exposure in HFIR.

The low gas atom generation rates associated with neutron irradiation result in large theoretical inter-bubble spacings; the predicted bubble densities lie in the range \( 2.8 \times 10^{12} \text{ m}^{-2} \) to \( 3.6 \times 10^{11} \text{ m}^{-2} \) which are significantly lower than the measured bubble densities reported here (typically \( 1 \times 10^{15} \text{ m}^{-2} \)). Farrell and Packan report similarly high densities at grain boundaries in dual-ion irradiated Nimonic PE16 alloy (114)(see table 4.5) Bennetch and Jesser (30) recently compiled results from neutron- and ion-irradiated stainless steels and from their analysis show interbubble spacings at grain boundaries in the range 20-100nm for helium-ion irradiation but spacings as large as 500-5000nm for neutron irradiation at 600°C (30). These results are entirely consistent with the predictions of the model for bubble nucleation.

The helium bubble density at grain boundaries is an important parameter in numerous helium embrittlement models (24-27) so it is important that the nucleation density of bubbles is known for the case of fusion neutron irradiation. The gas generation rate during fusion neutron irradiation of 316 stainless steel is estimated as \( 3.4 \times 10^{-6} \text{appmHes}^{-1} \) (6). On the basis of the nucleation model bubble densities of the order of \( 10^{12} \text{ m}^{-2} \) are expected (assuming the capture volume of a grain boundary is 20nm wide). This bubble density is the homogeneous nucleation density. It may be that nucleation at grain boundaries in commercial alloys will be determined by heterogeneous nucleation at grain boundary precipitates,
particularly if the precipitate density is greater than that predicted for homogeneous bubble nucleation. Other factors may also contribute to the density of bubbles at grain boundaries during neutron irradiation at high temperatures such as bubble migration and bubble sweeping by dislocations (27). The contribution of these mechanisms to the total bubble density is not clear but will be a function of both applied stress and temperature.

7.4.3 THE TEMPERATURE DEPENDENCE OF BUBBLE DENSITY

The model for bubble nucleation is consistent with experimental observation if it is assumed that helium diffuses by a vacancy-type mechanism at a rate equivalent to grain boundary self-diffusion. Figure 7.4 shows the measured bubble density as a function of temperature for those grain boundaries with no resolvable GBDs (see table 6.6). There is a slight temperature dependence, the bubble density decreasing with temperature. The two full lines represent the model prediction; the bubble density was calculated assuming that the diffusion coefficient for helium at grain boundaries is described either by equation 7.15 or equation 7.16. The gas atom arrival rate \( G_B \) was a function of the implantation temperature (see table 6.12) but due to limited experimental data for the temperature dependence of the capture volume, the gas arrival rate was estimated using linear extrapolation between the data points at 25°C intervals.

The measured bubble densities fall between the predictions of the model (figure 7.4) and the observed trend is successfully predicted but the temperature dependence is weaker than that calculated. The
scatter in the results and an uncertainty as to the exact temperature
dependence of both $D_B$ and $G_B$ make it unrealistic to make any
further quantitative deductions from the data. The magnitude of the
bubble density ($1 \times 10^{15} \text{m}^{-2}$) is, however consistent with a slow
vacancy migration mechanism for helium at grain boundaries over the
temperature range 450°C to 600°C rather than by rapid diffusion
by an interstitial mechanism.

7.4.4 THE EFFECT OF DISLOCATIONS AT THE INTERFACE

The presence of visible GBDs tends to increase the bubble density
at all implantation temperatures (section 6.3.4). The observation of
bubble alignment along GBDs substantiates the conclusions of Braski et
al (100) and of Kesternich and Rothaut (105) that GBDs act as
preferential nucleation sites for helium bubbles. In their work,
however, it was not clear that the observations were due to
preferential nucleation or to bubble/dislocation motion since their
experiments involved long annealing periods often under an applied
stress. The short implantation times used in this work (<20 minutes)
were insufficient to allow significant bubble migration (section 7.3).
It is reasonable to conclude that helium bubble nucleation does occur
preferentially at GBDs. The mechanism for preferential bubble
nucleation described by the nucleation model (section 7.4.1) is that
helium atoms are free to diffuse in the boundary plane until they
become bound at a GBD. Then diffusion is limited to one-dimension
along the dislocation core. This mechanism requires a significant
He-GBD binding interaction. A binding energy was predicted
theoretically for edge lattice dislocations in various BCC metals
(44, 45).
Consider the bubble nucleation model in the presence of GBDs (figure 7.2); examples of both case a) \( d > 2r_2 \), figure 6.26) and case b) \( d < 2r_2 \), figure 6.25 and 6.26) were identified. Nucleation between GBDs occurs when it is more likely that helium atoms will meet between the dislocations than diffuse to them; this occurs when the dislocation spacing \( d > 2r_2 \). This suggests a limit for case a where \( d = 2r_2 \). Realistically, the critical GBD spacing may be larger than this since the diffusion of helium atoms in the boundary plane will be directed to the GBDs by a long-range interaction with the stress field of the dislocation (42,43).

A number of interfaces were characterised in terms of the bubble density, GBD spacing and Burgers vector (section 6.3.4) from discs irradiated at 600°C. Three high-angle interfaces were analysed which showed the alignment of bubbles along GBDs (figure 6.25) and were examples of case b \( d < 2r_2 \). The areal bubble density at these interfaces is plotted as a function of measured dislocation spacing in figure 7.4. The full lines show the theoretical bubble density given by equation 7.12, calculated with assumed ratios of \( G_B / D_D \). The experimental data points show a decrease in bubble density with increased dislocation spacing and the theoretical curve reflects this trend well with \( G_B / D_D = 3.2 \times 10^{10} \text{m}^{-2} \). This implies a diffusion coefficient for helium along GBDs of \( 1.3 \times 10^{-14} \text{m}^2\text{s}^{-1} \) which should be compared with the two-dimensional diffusion coefficient of helium at grain boundaries, \( D_B = 2 \times 10^{-14} \text{m}^2\text{s}^{-1} \). From these diffusion coefficients it appears that helium diffuses as rapidly along GBDs as in the interface and both diffusion paths are slow compared to interstitial helium migration within grains (see equation 7.14). In a recent review
Balluffi (40) showed that, in general, diffusion at grain boundaries occurs at about the same rate as that along matrix dislocations which is in agreement with the result reported here for helium diffusion along GBDs. In contrast, atomistic calculations (37) show that the migration energy of helium along perfect, edge lattice dislocations in BCC metals is not significantly different from that for interstitial migration in the bulk crystal. Thus the gas atom retains considerable mobility along the dislocation core. The low diffusion coefficient for helium along GBDs reported here is in apparent contradiction to these calculations. However, a GBD will not be perfectly straight but will contain jogs, at which helium atoms will be strongly bound (see table 2.1) thereby restricting gas atom mobility. Furthermore, Balluffi and Granato (214) argue that diffusion of interstitial atoms along dislocations may be slow due to sites present in the core where interstitials are tightly bound; the trapped atoms only diffuse as fast as a vacancy mechanism will allow. This argument is identical to the case for slow diffusion of interstitial atoms at grain boundaries. The mobility of helium along GBDs is about the same as that at grain boundaries. It was previously reported that the helium diffusion coefficient along GBDs is an order of magnitude greater than that at grain boundaries (238). This discrepancy is due to an error in the previous analysis.

Point e in figure 7.4 represents the bubble density at the low-angle interface (facet C in figure 6.24). The dislocation spacing represents the coarsest array of dislocations which is necessary to account for the measured misorientation (three arrays were required to accommodate the total misorientation). Note that no fine dislocation arrays were resolved at the interface. For this facet the bubble
density is not enhanced. The dislocations are so close that the strain fields have cancelled and the dislocation cores have effectively touched. Thereby, there are no identifiable GBD traps for helium atoms and migration is not restricted to one dimension alone. A general point emerges from this observation; the structure of grain boundaries (both high- and low-angle interfaces) can always be represented geometrically by arrays of GBDs (193). However, when the deviation from a coincidence orientation is large the GBD spacing becomes so small that the remaining cores no longer act as discrete lines of helium-binding sites. There must be a critical dislocation spacing \( (d_c) \) at which the dislocation model of the interface has no physical significance; the interface then becomes essentially two-dimensional again with respect to helium migration and bubble nucleation will occur at the spacing \( 2r_2 \) (equation 7.8). The absolute value of the critical GBD spacing will probably depend on the boundary type and Burgers vector of the GBDs. The one dimensional diffusion model for bubble nucleation at GBDs breaks down at small dislocation spacings. At large dislocation spacings \((d>2r_2, \text{ case a})\) bubbles nucleate between the GBDs and again, the bubble density is best given by the two-dimensional nucleation model. In the limit \((d=2r_2)\) the dislocation spacing \( d=34 \text{nm} \) (since \( r_2=17 \text{nm} \) for a nucleation density of \(1 \times 10^{15} \text{m}^{-2} \)) represents the dislocation spacing at which bubble nucleation becomes significant (neglecting any long-range interaction of helium with a dislocation). This is entirely consistent with experimental observation since all bubbles are aligned along visible GBDs when the spacing is as large as 29nm (figure 6.25).

A further point concerns the magnitude of the Burgers vector of...
GBDs. The only requirement of the nucleation model is that there be sites along the GBD at which helium atoms are bound more strongly than in the rest of the interface. The Burgers vectors of the visible dislocations reported in this work were all relatively large \((b>0.26a)\) and hence a large helium-dislocation binding interaction would be expected. If the Burgers vector of the GBDs is small (as for some \(b_1^\text{a} \text{ and } b_2\) type dislocations) then the binding energy of a helium atom to the dislocation will be small (equation 2.1(42)). It is likely that the magnitude of the strain field affects both visibility in the TEM and the presence of significant helium traps; thus, enhancement of bubble nucleation is only identified when GBDs are resolvable.

Preferential nucleation of bubbles at GBDs is a result of both binding and migration of helium atoms along the dislocation. Braski et al. (110) tentatively suggested that this preferred nucleation could explain the variation of bubble density from boundary to boundary since the GBD structure will vary as a function of misorientation. Indeed, the work here supports this argument for dislocation spacings in the range \(d_c<d<2r_2\). The dislocation model for grain boundaries is not physically relevant for small dislocation spacings where the strain fields cancel out. The cores of the GBDs overlap and helium mobility is no longer restricted to one dimension; the interface is essentially a homogeneous array of helium binding sites where two dimensional migration is possible. The remaining core component may, however, impose restrictions on the mobility of helium resulting in anisotropy of the boundary diffusion coefficient. Any anisotropy will modify the probability of a nucleation event occurring (two helium atoms meeting) and the resultant bubble density will
deviate from that predicted by the two-dimensional (isotropic) diffusion model. Furthermore, since the structure of grain boundaries varies as a function of misorientation at the atomic level it is reasonable to assume that the diffusion coefficient of helium is also dependent on misorientation. In terms of the nucleation model, the nucleation density of bubbles at grain boundaries is a function of the gas atom diffusion coefficient so some boundary to boundary variation in density should be expected.

Kesternich and Róthaut (105) recently argued that interfacial dislocations at TiC/austenite interfaces enhance the nucleation of helium bubbles by acting as strong helium trapping sites. A dislocation array with a spacing of about 1nm was proposed, although this could not be resolved in the microscope. From the present study it is not clear that such closely spaced dislocations will enhance the nucleation of helium bubbles since the strain fields of such dislocations will cancel out. Although there are no long range strain-fields at the interface the core component may act as an efficient trapping site for helium; the cores of GBDs may be different from those at interphase interfaces.

Grain boundary dislocations were decorated with a high density of helium bubbles. In contrast bubbles were rarely aligned along dislocation segments within grains (eg. figure 6.2). The binding energy of a helium atom to a lattice dislocation is expected to be higher than that at a GBD since the Burgers vector of lattice dislocations is greater than that of GBDs (193). The absence of resolvable bubbles at lattice dislocations must, therefore, be due to a lower flux of helium atoms to the dislocation line. For GBDs,
helium atoms are trapped by the interface which acts as a planar trap. The interface essentially directs the flux of helium atoms to the GBDs. In contrast, the flux of helium atoms to lattice dislocations (only linear traps) is a result of three dimensional diffusion within grains and only those helium atoms which are implanted in the vicinity of dislocations will eventually become trapped. Thus, the flux of helium atoms to lattice dislocations is expected to be lower than that for GBDs.

7.5 ADDITIONAL FEATURES OF BUBBLE NUCLEATION AT GRAIN BOUNDARIES

The nucleation characteristics of helium bubbles at incoherent twin interfaces showed additional features of interest, namely that associated with different regions of black-white contrast (figure 6.28) and the nucleation of bubbles in the presence of extrinsic dislocations (figure 6.29). The black-white contrast may be attributed to the presence of partial GBDs. In the previous discussion all interfacial dislocations were perfect, secondary GBDs which accommodate the misorientation from exact coincidence and preserve the structure of the boundary. Partial GBDs delineate regions of different rigid body translation in near coincidence boundaries; these translations lead to a more stable atomic configuration at the interface and there may be several, symmetry related translations (215). Partial GBDs were first reported at incoherent twin interfaces in aluminium (215). Black-white contrast was observed at incoherent twin interfaces in stainless steel (216) and in a Σ9 related interface in a Cu-Si alloy (217); it was proposed that a partial GBD separated the regions of different translation. In each case, the black-white contrast was visible with a common diffraction vector.
Foll et al propose that this contrast arises due to a phase shift in the electron beam which is related to the magnitude of the translation vector (216). Since the translation vector has a component which lies outside the boundary plane the different regions are visible if imaged with a common diffraction vector (218). Details of the contrast mechanism remain unsolved (216,218).

Determination of the Burgers vector of partial GBDs is non-trivial involving comparison of experimental and computed micrographs (215). An analysis is not performed here. It is interesting to note that bubble nucleation is favoured in one translation state rather than the other (figure 6.28) which may be interpreted in terms of the nucleation model as a differential mobility of helium. Where migration is slow (more binding sites) the nucleation density is high, whereas if the interfacial structure allows rapid diffusion the nucleation density will be low. Note also that bubbles decorate the partial GBDs which delineate the different translation states.

Figure 6.29 shows the nucleation of helium bubbles at another twin interface. Bubbles do not show preferential nucleation along the dislocations which are visible in figure 6.29c. Since the dislocations are extrinsic in nature it is not clear whether the dislocations were present during implantation or were introduced during subsequent specimen preparation. In all the interfaces studied there was no unambiguous evidence for the preferential nucleation of helium bubbles at extrinsic dislocations. Varin (219) recently studied the relaxation of extrinsic GBDs at grain boundaries during hot stage experiments in the microscope by observing the loss of
strain contrast. A number of metals were studied including austenitic stainless steel, in which extrinsic GBDs became invisible in the TEM after 10 to 40 seconds at temperatures in the range 430°C to 590°C. The relaxation mechanism of these dislocations remain unclear but may be due to core widening (220) or dissociation into secondary GBDs (221). Clearly, it may be that extrinsic dislocations anneal out during the heating period of about 20 minutes prior to helium implantation. It is unreasonable to propose preferential nucleation of bubbles at extrinsic GBDs since the strain field associated with the dislocation becomes ineffective as a helium trapping site at high temperatures. In contrast, Kesternich and Rothaut (105) report preferential bubble nucleation on extrinsic GBDs in an austenitic stainless steel after annealing at 700°C during creep experiments. Due to the uncertainty of when the dislocations are introduced it is not possible to comment further on these observations.

7.6 SUMMARY

It is not possible to account for all the implanted helium in equilibrium sized bubbles either within grains or at grain boundaries which implies that helium is trapped sub-microscopically in small bubbles or in helium-vacancy clusters. Some overpressure in the bubbles is also likely although this is not sufficient to generate detectable strain fields in the electron microscope. Bubble nucleation at grain boundaries is complete in the early stages of implantation and is consistent with a model which assumes that a di-helium complex forms a stable bubble nucleus.
The nucleation model was used to explain the dependence of bubble
density at grain boundaries on the gas implantation rate, temperature
and on the presence of dislocation arrays in the interface. Bubbles
nucleate preferentially at GBDs which are resolvable in the TEM where
helium atom diffusion is limited to one dimension along the cores of
GBDs. A significant helium-GBD binding interaction was inferred.
Sub-microscopic GBD arrays do not appear to enhance the nucleation
density of helium bubbles. The model for helium bubble nucleation was
derived assuming steady-state diffusion conditions at the interface
and enabled the estimation of the rate of helium migration at grain
boundaries and along GBDs.

Helium atom diffusion at grain boundaries and along GBDs is slow
relative to helium interstitial diffusion within grains. The helium
diffusion coefficient at grain boundaries is of the order of the
self-diffusion coefficient which implies that helium diffusion at
grain boundaries is by a vacancy-type mechanism. The diffusion
coefficient of helium along GBDs is approximately the same as that at
grain boundaries. Boundary to boundary variation in the bubble
nucleation density at grain boundaries is due to the variation of the
migration rate of helium with misorientation; anisotropy of boundary
diffusion may also contribute to some variation in bubble density.
The bubble nucleation model was used to estimate the homogeneous
nucleation density of bubbles at grain boundaries during neutron
irradiation where the gas generation rates are low compared to
helium-ion implantation. The model prediction was consistent with
reported grain boundary bubble densities in neutron irradiated
materials. When applied to the case of fusion neutron irradiation the
model predicts a homogeneous bubble nucleation density of the order of
$10^{12}$ m$^{-2}$ in stainless steels irradiated at 600°C. The roles of partial GBDs and of extrinsic GBDs in the nucleation of helium bubbles are not clear and should be the subject of future research.
CHAPTER EIGHT. DISLOCATION LOOPS AT AND NEAR GRAIN BOUNDARIES

Heterogeneous dislocation loop nucleation was observed at coherent twin interfaces and in the vicinity of some grain boundaries (section 6.4). A number of points emerge from these observations regarding the role of grain boundaries during irradiation.

8.1 DISLOCATION LOOPS AT TWIN BOUNDARIES

8.1.1 THE BURGERS VECTOR OF DISLOCATION LOOPS AT TWINS

Interstitial dislocation loops nucleate and grow at coherent twin interfaces during ion-implantation. The Burgers vector of the loops is of the type \( \mathbf{b} = \frac{a}{3}[111] \), which is also the Burgers vector of loops which nucleate within grains. This vector is a translation vector of the \( \Sigma 3 \) DSC-lattice; the dislocations are therefore perfect GBDs and preserve the structure of the interface. A model of an interstitial loop at a coherent twin interface is shown in figure 8.1. The twin plane is indicated by a subscript T. The extra twin plane of interstitials forming the dislocation loop is indicated by a subscript L. The twin plane is effectively stepped up two (111) planes, but there is no extrinsic fault as would be the case in the matrix. Removal of the stacking fault provides the driving force for an unfaulting reaction in matrix loops; the unfaulting occurs by the passage of two Shockley partial dislocations, one above and one below the extra atomic plane (section 4.2). This mechanism is modified for \( a/3<111> \) loops at twin interfaces as shown in figure 8.1. The passage of only one Shockley partial dislocation merely moves the reflection plane down, reducing the step height to one (111) plane by a reaction
of the type:
\[ \frac{a}{3}[111] + \frac{a}{6}[11\bar{2}] = \frac{a}{2}[110] \]

An \( \frac{a}{2}[110] \) dislocation remains whose Burgers vector is out of the plane of the diagram. It is not clear that such a reaction is energetically favourable since the energy gained by a reduction in step height (222) must be balanced by an increase in strain energy of the dislocation loop since there is an increase in the magnitude of the Burgers vector of the dislocation. It is difficult to conclude whether the driving force for dissociation is significant because little is known of the magnitude of interfacial step energies. The nucleation of the dissociation reaction is easier in the twin case where only one Shockley partial dislocation is needed. During dual-beam irradiation, however, matrix loops were found to dissociate and climb, creating dislocation line segments (section 6.2.2) whereas the loops at twins retained their \( \frac{a}{3}[11\bar{1}] \) Burgers vector (figure 6.30c). From this observation it appears that the dissociation reaction is favoured for matrix loops and is evidence of the large driving force for dissociation of matrix loops relative to loops at twins. The driving force for the dissociation reaction is the energy gained by removing the stacking fault. Since there is no stacking fault associated with \( \frac{a}{3}[11\bar{1}] \) dislocation loops at twins the only energy gained by dissociation would be due to the reduction in step-height.
8.1.2 INTERSTITIAL ATOM-TWIN INTERACTION

Norris first argued that coherent twin interfaces act as biased interstitial absorbers from his observations of enhanced void growth in the vicinity of (111) twin interfaces in electron irradiated nickel (171) but dislocation loops were not reported. In this work, loop nucleation at coherent twin interfaces was associated with a 100nm zone denuded of loops on both sides of the interface. This is evidence of a positive binding interaction between migrating interstitials and the twin interface because interstitials are lost to the boundary. This results in a local reduction in the interstitial concentration to a level below the supersaturation required for loop nucleation. King and Smith (157) also report triangular loops at twin interfaces in electron irradiated copper and aluminium. They proposed two possible mechanisms for preferential loop nucleation at the interface which do not involve interstitial-twin binding interaction. First, the loop at a twin does not enclose a region of stacking fault, thereby the nucleation of dislocation loops at twins is energetically more favourable than that within grains. Although there is a low nucleation barrier this explanation does not provide a mechanism for loop nucleation. The second argument proposed by King and Smith (157) is that more interstitial atoms are produced at a twin interface than elsewhere. Focussed collision sequences along the \( \langle 110 \rangle \) directions in the matrix which do not lie in the twin plane lie parallel to the \( \langle 114 \rangle \) directions in the twin. Thus a collision sequence must end at a twin interface. This argument is sufficient to explain why there is a high density of large dislocation loops in the vicinity of coherent twin interfaces but it is necessary to further argue that there is a significant interstitial-twin binding
interaction to explain why all the loops nucleate on the (111) twin plane. Without a binding interaction interstitial atoms would be free to migrate away from the interface and nucleate loops elsewhere.

The presence of a zone denuded of loops coupled with the preferred nucleation of loops at twin interfaces is consistent with a significant positive binding interaction between interstitials and the twin interface. No interaction would be predicted by considering nearest-neighbour interactions, since to this approximation the twin boundary has the same stacking as the matrix. However, lattice calculations show that self-interstitial atoms in FCC metals adopt either a <100> split-dumbell configuration (233) or a <110> split-configuration (224). It becomes necessary to consider second-nearest neighbour interactions to account for a positive binding interaction. Akhter and Crocker (224) recently used atomistic calculations (with nickel-nickel potentials) to study the interactions of interstitial atoms with coherent twin boundaries in FCC metals. The calculations showed that the binding energy of a <110> split interstitial to the interface was 0.53eV. Furthermore, a mechanism for the nucleation of interstitial dislocation loops was proposed, whereby migrating <110> split interstitials within grains approach a coherent twin interface and rotate into one of the three <110> directions parallel to the (111) twin plane. Although the interstitials are effectively bound to the interface they are free to migrate in the plane of atoms parallel and adjacent to the boundary with a migration energy of only 0.04eV. This low migration energy implies rapid interstitial diffusion at the interface and is in apparent contradiction to the slow migration of interstitial atoms at general grain boundaries as proposed by Balluffi (40). However, rapid
diffusion of interstitial atoms at coherent twin interfaces may reflect the special nature of the (111) twin plane. Interstitial atoms at a twin interface are restricted to migration within the boundary plane and are, therefore, much more likely to meet and interact with each other than in the three-dimensional crystal. The binding energy of two <110> split interstitial atoms was calculated as 1.11eV (224) so when two interstitial atoms meet at the interface they form a stable di-interstitial pair which is the nucleus for a dislocation loop. The calculations of Akhter and Crocker (224) are entirely consistent with the observations made here. Irradiation induced interstitials are free to migrate within grains but are trapped at coherent twin interfaces. A bound interstitial, however, retains significant mobility in the boundary plane, thereby nucleation of interstitial dislocation loops is possible.

In section 6.3.1 it was shown that coherent twin interfaces do not act as preferential sites for the nucleation of helium gas bubbles. Helium may exist as a trapped substitutional atom or as a mobile interstitial atom and it is necessary to determine whether a helium-twin binding interaction is likely. The lattice strain associated with interstitial helium atoms is large but unlike self-interstitial atoms they adopt an octahedral position in the lattice rather than a split configuration (32). Since the coherent twin interface is essentially close packed it presents an array of octahedral sites identical to those in the matrix, so from nearest neighbour considerations, no helium-twin binding interaction is postulated. A similar argument holds for substitutional helium atoms but these are effectively immobile and cannot contribute significantly to bubble nucleation. The observation that helium bubbles do not
nucleate preferentially at coherent twin interfaces is consistent with there being no significant binding interaction between a helium atom and the twin interface. An observation made in chapter six was that helium bubbles nucleate preferentially at interstitial dislocation loops. From nearest-neighbour considerations the faulted loop presents an array of octahedral sites in much the same way as the coherent twin interface. However the bubble nucleation behaviour is markedly different. It may be that the bounding dislocation acts as a prefered nucleation site for bubbles but climbs around the bubble nucleus during irradiation. Alternatively, a significant translation may exist at a faulted dislocation loop which is not predicted from nearest-neighbour considerations and which may contribute to a significant helium atom-fault binding energy.

8.1.3 THE SHAPE OF LOOPS AT TWIN BOUNDARIES

The shape of interstitial dislocation loops at twin interfaces was sensitive to the irradiation conditions (figure 6.30); the loops were approximately triangular after chromium-ion irradiation alone but exhibited three extended lobes after dual-beam irradiation. Dual beam irradiation to a dose of 3.5dpa resulted in growth and coalescence of the loops which formed irregular shapes. The triangular loops are similar to those reported by King and Smith (153) and the general three-fold symmetry is inherent in the coherent twin structure of FCC metals. This does not explain the three lobed nature of the larger loops in which the dislocation line length is almost twice that which is strictly necessary to bound the same number of interstitials in a circular loop. Three-fold symmetry has also been reported for both vacancy-type and interstitial dislocation loops when they form as
double loops within an outer faulted loop in several FCC metals (eg. 225-228).

Two mechanisms have been proposed to explain the regular, geometric shapes of dislocation loops. First, the Frank partial which bounds the loop can dissociate into a stair-rod dislocation and a Shockley partial on an intersecting \{11\} twin plane. This mechanism was proposed for matrix dislocation loops (226) and for triangular loops at faulted dislocations. However the model requires perfectly straight, geometric shapes and remains unconvincing because of the generally curved nature of the sides of the triangles (226,228). The second mechanism involves the relative ease of jog formation and jog migration (229). During loop growth an interstitial atom forms a jog on the perimeter of the loop and the jog migrates by the addition successive interstitials. The migration of jogs is much easier than the formation of new jogs because of the high formation energy. As a result, the jogs migrate to the corners of the growing loop and few exist along the dislocation line; the loop tends to be bounded by straight lines in the close packed directions. It is not a strict requirement that dislocations be bounded by perfectly straight dislocations. It seems likely that jog mobility/nucleation controls the shape of the triangular loops at coherent twin interfaces since the dislocation lines are not perfectly straight. The irregular three-lobed dislocation loops exhibit virtually no linear segments so a dissociation mechanism controlling the loop shape is improbable.

Irregular shaped dislocation loops within grains were observed (figure 6.11) after both helium-ion and dual-ion irradiation. The larger faulted loops take the form of rosettes. No such loops
developed during chromium-ion irradiation alone. Similar, rosette shaped loops have been reported in a variety of materials which include a dual-ion irradiated Nimonic alloy (230) and electron irradiated gold (231), stainless steel (232) and iron (233). Junqua and Grilhe developed a general model to describe the growth of irregular shaped dislocation loops (234). On the basis of their model, the circular form of growing dislocation loops becomes unstable above a critical radius. The critical radius for the unstable growth of perturbations in the dislocation line is small when the ratio \( D_p/D \) is small (where \( D_p \) is the dislocation pipe diffusion coefficient and \( D \) is the bulk diffusion coefficient). In metals, the bulk diffusion coefficient for interstitial atoms is very high whereas interstitial diffusion along the cores of dislocations may be slow due to sites of high binding energy along the core (214). The ratio \( D_p/D \) is intrinsically low for growing interstitial loops.

In the work reported here, dislocations within grains and at twin boundaries exhibit irregular growth during the implantation of helium. Considering the analysis outlined above it is possible to postulate the role of helium in the formation of irregular shaped dislocation loops. If the flux of interstitial atoms to a growing loop is high then pipe diffusion around the loop is insufficient to maintain a stable loop geometry. At loop sizes below the critical radius, pipe diffusion maintains a stable loop geometry; but for large loops any perturbations will be stable against pipe diffusion and loop growth will be irregular. The observations of large rosette shaped interstitial loops in electron irradiated metals can be explained on the basis of a high flux of interstitials to the growing loops. Similarly, simultaneous helium implantation may result in high fluxes
of interstitials to loops; helium was seen to enhance the density and the size of matrix dislocation loops which may be interpreted in terms of a reduction in the point defect recombination rate due to helium-vacancy interactions (150).

Helium atoms may play a more direct role in creating instability in the growth of interstitial dislocation loops. A high concentration of helium atoms at the dislocation core could inhibit pipe diffusion of interstitials, so reducing the ratio $D_{\text{p}}/D$ even further and enhance the development of irregular dislocation loops. In other words, the presence of helium at the core may alter the relative ease of jog formation and migration and lead to irregular shaped loops.

Shaw et al (230) observed irregular growth of interstitial dislocation loops in Nimonic PE-16 alloy during dual-beam irradiation. The observation was attributed to pinning of the growing dislocation line by $\gamma'$ precipitates although it was not clear from their micrographs that precipitates were present along the dislocation line. No such precipitation was observed in the ternary alloy used in this work and no evidence of $\text{M}_{23}\text{C}_6$ precipitation could be found (either in the micrographs or in the diffraction patterns) in these low dose specimens. The possibility exists that small helium bubbles may pin the dislocation line. Bubbles were always associated with the faulted region of dislocation loops rather than with the bounding dislocation line (figure 6.2 and 6.11) and it is concluded that bubbles do not act as obstacles to the growing dislocation line.

It is now possible to put forward an explanation for the three-lobed nature of interstitial dislocation loops at twin
interfaces. Interstitial atoms retain significant mobility when bound to the interface (224) but pipe diffusion along dislocations may be slow (214). The ratio $D_p/D$ is intrinsically small. Implanted helium atoms will act either to reduce the interstitial migration rate around the dislocation or to enhance the flux of interstitials to the growing dislocation; thereby reducing the ratio $D_p/D$ still further. In addition, interstitial migration in the boundary plane is likely to be anisotropic (234) with maxima in three symmetry related directions. The effect will provide an extra driving force for the growth of irregular shaped dislocation loops since pipe diffusion will be insufficient to maintain a stable loop geometry against the anisotropic flux of interstitial atoms.

Sumida et al (233) proposed a similar mechanism for the growth of irregular loops in electron irradiated iron. The corners of the loops grew more rapidly than the edges and the loops eventually developed petal-like shapes. A similar argument was proposed for irregular loops in electron irradiated gold (231). These observations were attributed to the long-range interaction of point defects with the strain field of the dislocation which results in an enhanced flux of interstitials to the corners of the loops. A necessary criterion for this mechanism is that the rate of interstitial pipe diffusion is insufficient to allow migration of the incoming defects around the dislocation line. This mechanism could further contribute to the growth of lobes from the corners of triangular loops at twin interfaces.

Once a three lobed loop has formed, additional factors may act to stabilise it. Since each lobe is effectively a small dislocation
dipole the three lobed shape could be stabilised by the attractive interaction between equal but oppositely directed dislocations on each side of the lobe (figure 6.33). This option is not easily available to the inner triangle of a double loop because of the proximity of the outer hexagon and the directional nature of the vacancy flux to the centre of the defect (235).

The above explanation for the shape of three lobed loops essentially involves a kinetic argument based on the diffusion of interstitial atoms followed by a stabilisation of the resultant shape by dipole forces. Any alternative argument in terms of an equilibrium shape would need to invoke a large anisotropy of either (or both) dislocation line energy or twin boundary step energy. There is no evidence that either of these effects would be large enough to account for the presence of twice as much bounding dislocation as is strictly necessary.

8.2 HETEROGENEOUS LOOP NUCLEATION NEAR GRAIN BOUNDARIES

Interstitial dislocation loops nucleate and grow heterogeneously adjacent to some grain boundaries (section 6.4.2). The loops nucleate in bands on one side of the interface at a range of 15-30nm from the interface (figure 6.35). A similar observation was made by Farrell who reported unfaulted dislocations in the immediate vicinity of some grain boundaries in neutron irradiated aluminium (162) but no explanation was given. A common feature of all the interfaces which exhibit this effect is that the grain above the interface (with respect to the ion beam) was oriented such that the foil normal was parallel to a <110> direction (figure 6.36). Heterogeneous loop
nucleation always occurred below the grain boundary with respect to the ion beam.

These observations are consistent with the following argument; a $\langle 110 \rangle$ texture is common to rolled and annealed austenitic stainless steels (236) so a number of grains in a 3mm disc specimen will be oriented with a $\langle 110 \rangle$ direction parallel to the direction of the incident chromium-ion beam. The $\langle 110 \rangle$ directions are channelling directions in FCC metals (237) and the incident chromium-ions can penetrate the grain losing only a small amount of energy due to glancing collisions along the channel. However, if a grain boundary is oriented such that it crosses the paths of channelling ions (figure 6.36) the ions are no longer presented with a favourable direction for channeling. Consequently, the ions lose their remaining energy within a short distance on the opposite side of the grain boundary. The loops lie at a distance of 15-30nm from the boundary. This is consistent with the damage peak of 70nm (figure 5.8b) for 380keV chromium-ions since the peak must be resolved along the boundary normal to attain the distance of loop nucleation away from the boundary. In addition, some energy is lost in the channeling grain by displacement events so the channeled ions will have an energy less than 380keV.

This argument is similar to that used by King and Smith who proposed that coherent twin interfaces act as barriers to the propagation of focussed collision sequences (157) which propagate along the $\langle 110 \rangle$ directions in FCC crystals. For focussed collisions, the energy transferred is small so a defocussed interstitial atom will not penetrate the adjacent crystal. For the coherent twin interface...
the interstitials migrate in the boundary plane and interstitial dislocation loops nucleate and grow. In the general case of high angle grain boundaries the interstitial atoms are absorbed into the boundary structure (154). In contrast, channeling atoms retain much of their original energy; when dechanneled at a grain boundary the atom will penetrate the adjacent grain causing displacement damage. Eventually the dechannelled atom will come to rest at a distance defined by the ion-range.
1. Helium bubbles nucleate preferentially at all grain boundaries except coherent twin interfaces. Preferential nucleation is due to a significant binding interaction between helium atoms and the interface. No such interaction is envisaged at twin interfaces.

2. The nucleation density of helium bubbles at grain boundaries increases with helium implantation rate, decreases with temperature but was insensitive to the He/dpa ratio during dual-beam irradiation. The presence of resolvable dislocation arrays at grain boundaries enhances the bubble nucleation density; bubbles are aligned along visible GBDs.

3. The alignment of helium bubbles along visible GDBs is evidence for preferential nucleation at these sites; a binding interaction between a helium atom and a GBD is also inferred. Secondary intrinsic GBDs enhance the nucleation density of helium bubbles when the dislocation spacing is set between limits. The upper limit is set by the spacing at which nucleation between dislocations can occur. At GBD spacings below this limit all bubbles nucleate on GBDs and the bubble density increases as \((\text{dislocation spacing})^{-3/4}\) until the GBDs are too close to be visible as discrete entities in the TEM. The lower limit to the dislocation spacing is not clearly defined (due to the limit of resolution in the TEM) but occurs when strain field cancellation and core overlap reduces the effectiveness of a GBD as a trap for helium.
consistent with experimental results if it is assumed that helium atoms diffuse at a rate equivalent to grain boundary self-diffusion in austenitic materials. Thus helium diffusion at grain boundaries is slow relative to interstitial helium diffusion within grains. The estimated diffusion coefficients for helium at grain boundaries and along GBDs are consistent with a slow vacancy type mechanism similar to that for grain boundary self- and impurity-diffusion and are $2 \times 10^{-14} \text{m}^2\text{s}^{-1}$ and $1.3 \times 10^{-14} \text{m}^2\text{s}^{-1}$ respectively.

Boundary to boundary variation in bubble nucleation density can be accounted for by the variation of the helium diffusion coefficient with misorientation; anisotropy of boundary diffusion may also contribute to some variation in bubble density.

5. Helium bubble nucleation and growth at grain boundaries was insensitive to the He/dpa ratio during dual beam irradiation. In marked contrast, the density of bubbles within grains increased with displacement rate, with the result that a larger proportion of the implanted helium contributed to bubble growth during implantation. These observations were consistent with a detrapping mechanism, such as interstitial replacement, for helium which is ineffective at grain boundaries.

6. Bubble denuded zones about 100nm wide were present at grain boundaries after helium-ion implantation at 600°C. In contrast, the estimated helium capture volume was only 20nm wide (as implied from the size and density of bubbles at grain boundaries). It was concluded that some of the implanted helium is trapped within the bubble denuded zone in the form of helium-vacancy clusters.
7. The nucleation of helium bubbles within grains was highly heterogeneous. Many bubbles were associated with the faulted region of interstitial dislocation loops but few bubbles decorated line dislocations. From the size and density of bubbles within grains it was inferred that some of the implanted helium must be trapped sub-microscopically in small bubbles or in helium-vacancy clusters. An overpressure in the matrix bubbles is also likely but is not sufficient to generate detectable strain fields in the electron microscope.

8. Irradiation induced self-interstitial atoms can cluster as dislocation loops at coherent twin boundaries. The Burgers vector of these loops is \( \mathbf{b} = a/3\langle 111 \rangle \), but the dislocation does not bound a region of stacking fault (as for \( \mathbf{b} = a/3\langle 111 \rangle \) matrix loops). Rather, the twin plane is stepped up by two close packed planes. The presence of a loop denuded zone on both sides of the twin interface implies that there is a positive binding interaction between a self-interstitial atom and the interface.

9. The shape of interstitial loops at twin interfaces may be triangular (after chromium-ion irradiation) or three-lobed (after dual-beam irradiation). The three lobed shape can be explained in terms of the mobility of self-interstitial atoms in the boundary plane and around the dislocation core. Helium atoms may restrict interstitial pipe diffusion around the dislocation core or enhance the interstitial flux to growing dislocation loops by inhibiting point defect recombination.
10. Grain boundaries act as dechannelling sites. A \langle 110 \rangle texture in the rolled and annealed alloy presents numerous grains which are favourably oriented for channelling during ion-implantation. Incident chromium-ions are channelled along the \langle 110 \rangle directions until their paths are crossed by a grain boundary. The ions, which still retain much of their energy, penetrate the adjacent crystal causing displacement damage. Heterogeneous nucleation of interstitial dislocation loops results at a distance of 15-30nm from the interface.

11. The Harwell Dual Beam Facility was used to study the synergistic effects of helium-ion implantation and displacement damage on the nucleation and growth of helium bubbles at grain boundaries and within grains. The low energy capability of the facility (500keV maximum for the heavy ion) results in an irradiated zone near to the surface where the irradiation induced microstructures are dominated by point defect loss to the surface and by self-interstitial injection. Contamination from the vacuum system can also cause spurious precipitation effects.
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A major feature of neutron irradiation induced microstructures is the nucleation and growth of voids; void formation has been successfully reproduced during dual-beam simulations using high energy (>4MeV) accelerators. The Dual-Beam facility at AERE Harwell has a maximum capability of only 500keV; the resultant ion-irradiated layer is necessarily near a free surface (typically 200nm) where point defect loss may be important. Much of the ion-irradiated layer will also be influenced by injected self-ions (see Figure 5.8b) since, at low beam energies, the displacement damage peak and ion-implanted range peak overlap significantly. Theoretical and experimental evidence for the effects of self-interstitial injection and point defect loss was reviewed in Chapter 4 where it was clear that these effects can significantly reduce the swelling capability of metals.

A semi-quantitative approach (after Evans(153)) has been adopted to assess the effects of free surfaces and of self-interstitial injection in this study. The swelling rate due to bias-driven void growth can be derived from the basic equations:

\[ K_V = D_{CV} (a_v + a_d) + a_C C_v \]  \[ K_I = D_{CI} (a_v + a_d) + a_C C_I \]  

Where \( K_V \) and \( K_I \) are the generation rates of vacancies and interstitials; \( C_V \) and \( C_I \) are the point defect concentrations; \( a_v \) and \( a_d \) are the sink strengths of voids and dislocations and \( A \) is a dislocation bias term, \( a \) is the recombination coefficient.

The void swelling rate is the difference between the number of vacancies and the number of interstitials which reach voids. If the
recombination rate is negligible then the swelling rate can be written:

$$\frac{ds}{dt} = (D_C V - D_I C_I) a_v$$  \text{......A.3}$$

Which may be written:

$$\frac{dS}{d\phi} = \frac{a_v}{a_v + a_d} - \frac{a_v}{a_v + a_d}$$

Where $\frac{dS}{d\phi}$ is the fractional volume change, $S$, with displacement dose $\phi$ (dpa) (after Evans (153)). During ion-irradiation the interstitial generation rate is supplemented by the injection of self-ions. If the ion-injection rate is $I_I$, the total interstitial generation rate is $K_I + I_I$. Following the analysis of Evans (153), this can be written as $K_I (1 + 1/B)$, where $B$ is the ratio $K_I / I_I$.

As an extension to the analysis of Evans (153) the ratio of the recombination rate $(a_C VC_V)$ to the displacement rate $(K)$ can be defined as $C$, where:

$$C = \frac{a_C VC_V}{K}$$

Equations A.1 and A.2 can now be re-written to include the effect of self-ion injection as:

$$K = D_C V (a_v + a_d) + K_C$$

$$K_I (1 + 1/B) = D_I V (a_v + A a_d) + K_C$$

By substitution into equation A.3 we can derive:

$$\frac{dS}{d\phi} = \frac{(A - 1)(1 - C) - (y + 1)/B}{y + A/y + A + 1}$$  \text{......A.4}$$

Here, $y = a_v/a_d$. Equation A.4 is similar to that derived by Evans (153) but also includes the effect of point defect recombination. The terms in the equation are:

A, the dislocation bias term (typically 1.02 (137)).

B, the ratio of the displacement rate to the ion-injection rate.

C, the rate of point defect recombination (expressed as a proportion
of the point defect generation rate).

\( y \), the ratio of the total void sink strength to the total dislocation sink strength.

This swelling rate equation was used to assess the effects of self-ion injection and point defect loss to recombination on the swelling potential during dual-beam irradiation. To a first approximation, point defect loss to surfaces can be accounted for using the recombination term since the surface acts as a sink for both interstitials and vacancies (realistically, the rate of interstitial loss is greater than that for vacancies).

The dislocation-bias term was assumed to be 1.02 (typical of stainless steels at 600°C (137)). The ratio of the displacement rate to the ion injection rate was determined from figure 5.8b. Due to the variation of both the displacement rate and the implantation rate with depth, the ratio \( B \) decreases with depth from \( 10^4 \) to \( 10^2 \). A ratio of \( B=10^3 \) is used to demonstrate the significance of injected ions on the swelling potential of the alloy. The rate of point defect loss to recombination and to unbiased sinks is difficult to quantify. In this semi-quantitative analysis a variety of values for \( C \) are adopted in order to assess the significance of this factor.

The swelling rate was calculated as a function of the microstructural variable \( y \) (the ratio of the void sink strength to the dislocation sink strength) using equation A.4. Figure A.1 shows the calculated swelling rates for various values of the ratios \( B \) and \( C \). Curve 1 represents the maximum possible swelling rate where there is no interstitial injection (the \( B \) term in equation A.4 is zero) and
also no point defect loss to unbiased sinks \((C=0)\). The maximum swelling potential occurs when the capture cross section for voids is the same as that for dislocations \((y=1)\). Note that for extremes in either the void or dislocation densities \((y \gg 1 \text{ or } y \ll 1)\) the swelling rate reduces to zero; this corresponds to point defect loss dominated by either voids or dislocations. Curve 2 shows the additional effect of self-ion injection \((B=10^3)\). The maximum swelling potential is reduced as is the range of microstructures over which swelling is appreciable. Curves 3 and 4 show the effect of both self-ion injection \((B=10^3)\) and point defect loss to unbiased sinks \((C=0.5 \text{ and } C=0.8)\). Clearly, the combined effect of self-ion injection and point defect loss to unbiased sinks is to significantly reduce the maximum swelling capability of the alloy and to restrict the range of microstructures which exhibit significant swelling.

The above analysis demonstrates that significant reductions in the swelling response of the austenitic alloy can be expected during dual-beam irradiation due to both self-interstitial injection and point defect loss to the surface. In practice both of these factors will vary as a function of depth; any swelling observed will vary as a complex function of depth and will be atypical of the bulk material response to neutron irradiation. The low energy capability of the Harwell dual-beam facility restricts the successful simulation of radiation damage due to fusion neutrons. No voids were observed in this study; only a fraction of the implanted helium was accounted for in equilibrium sized bubbles so it is reasonable to assume that the cavities were gas-filled. However, void formation has been reported in stainless-steels after low energy ion-irradiation in the absence of continuous helium implantation \((\text{e.g. 178,202})\). During dual-beam
irradiation in this work a high density of bubbles nucleate and grow. If a large proportion of the implanted helium resides in sub-microscopic bubbles/clusters then these defects can act as the dominant sink for vacancies and interstitials (i.e. \( y \ll 1 \) in equation A.4). The bubbles grow only by the addition of gas atoms and not by bias-driven vacancy adsorption. A similar situation arises with the precipitation of \( \text{M}_{23}\text{C}_6 \); the precipitate-matrix interfaces act as recombination sites for point defects thereby reducing the swelling capability of the alloy (202).

There are a number of additional practical limitations associated with the dual-beam facility which restricts its use for void swelling studies appropriate to the fusion case. The helium/dpa ratio during irradiation is effectively controlled by the ratio of the ion-beam currents and ratios as low as 40 appm He/dpa are possible. It is not possible to attain the helium/dpa ratios appropriate to the fusion case (20 appm He/dpa); furthermore, the precipitation of \( \text{M}_{23}\text{C}_6 \) (due to carbon contamination) restricts the maximum attainable dose to <15 dpa. Due to the limitations outlined above, the dual-beam facility was used to study the synergistic effects of helium implantation and displacement damage with helium/dpa ratios in excess of 200 appm He/dpa and with the displacement dose below 10 dpa. Although these conditions do not simulate the fusion case it has been possible to assess the role of displacement damage in the nucleation and growth of helium bubbles at grain boundaries and within grains.
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   c). Dual-beam irradiation (3.5dpa, 200appmHe/dpa).

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FIGURE 6.35 Bright-field micrographs showing heterogeneous loop nucleation in the vicinity of a grain boundary. In b) the interface is tilted vertically and loop nucleation is seen to occur on one side of the interface only.

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FIGURE 7.1 Schematic illustration showing the dependence of helium mobility on the vacancy concentration in the vicinity of a grain boundary.
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   b). $d < 2r_2$, nucleation only on GBDs at a spacing $2r_1$.

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   0 Dual-beam irradiation.
   x 40keV helium ion implantation.
   + 70keV helium ion implantation.
   The full lines represent the predicted trend with the assumed helium atom diffusion coefficient:
   a). $5 \times 10^{-15} \text{m}^2\text{s}^{-1}$.
   b). $1 \times 10^{-14} \text{m}^2\text{s}^{-1}$.
   c). $2 \times 10^{-14} \text{m}^2\text{s}^{-1}$.
   d). $5 \times 10^{-14} \text{m}^2\text{s}^{-1}$.
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   a). $3.2 \times 10^{11} \text{m}^{-2}$.
   b). $3.2 \times 10^{10} \text{m}^{-2}$.
   c). $3.2 \times 10^{9} \text{m}^{-2}$.
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   a) $\Sigma 43a$-related interface.
   b) $\Sigma 29a$-related interface (section A).
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- 70 keV helium ion implantation.

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- c) $2 \times 10^{-14} \text{m}^2 \text{s}^{-1}$
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B). \(3.2 \times 10^{10}\) m\(^{-2}\).
C). \(3.2 \times 10^9\) m\(^{-2}\).

Experimental data points:

a) \(\Sigma 43a\)-related interface.
b) \(\Sigma 29a\)-related interface (section A).
c) \(\Sigma 3\)-related interface.
d) \(\Sigma 29a\)-related interface (section B).
e) Low angle interface.
FIGURE 8.1 A model of an interstitial dislocation loop at a coherent twin interface.
FIGURE A1.1 Theoretical curves showing the swelling rate as a function of the ratio of the void sink strength to the dislocation sink strength.
Dislocation loops at twin boundaries in an ion-irradiated austenitic alloy

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[Received 23 February 1982 and accepted 4 May 1982]

ABSTRACT

Dislocation loops having a three-lobe shape have been observed at coherent twin interfaces in an ion-irradiated austenitic alloy. The specimens were implanted with 380 keV Cr⁺ and 40 keV He⁺ ions at 700°C and the loops formed both in the matrix and at the twin boundaries were found to be interstitial in nature with Burgers vectors of the type a/3(111). The presence of a loop-denuded zone at twin interfaces provides evidence for a significant interaction between interstitials and the coherent twin boundary. The loop shape has been interpreted in terms of the relative rates of diffusion of point defects along the dislocation line and in the twin interface.

§ 1. Introduction

The nucleation and growth of dislocation loops in both ion- and neutron-irradiated materials are well documented phenomena and the role of dislocations in void swelling has been recognized for some years (Mayer and Brown 1980, Brown, Kelly and Mayer 1989). In f.c.c. metals one of the predominant secondary defects is the interstitial cluster formed by the insertion of a monolayer of atoms on a {111} plane so producing an extrinsic stacking fault. The faulted Frank loop can become unfaulted by a dissociation reaction of the type (Barnes 1961)

\[
\frac{a}{3}[111] + \frac{a}{6}[112] + \frac{a}{6}[121] = \frac{b}{2}[011]
\]

Two Shockley partial dislocations (one above and one below the extra plane) sweep across the loop to remove the fault. Dislocation loops may therefore be faulted or unfaulted depending on the irradiation conditions. Vacancy loops have similar geometry but the vacancy or interstitial nature of a loop can be determined by a Burgers vector analysis using a variety of techniques (Mazey, Barnes and Howie 1962, Maher and Eyre 1971).

The use of accelerated ion beams in simulation studies of neutron irradiation is now well established (Nelson 1978). The present work is part of a study using two particle accelerators simultaneously to simulate fusion neutron irradiation. This dual-beam technique is being used extensively in materials research for various fusion programmes (Farrell, Lewis and Packan 1978, Choyke, McGraner, Townsend, Spitznagel, Doyle and Verskytis 1979, Agarwal, Ayrault, Potter, Taylor and Nolfi 1979). In a fusion reactor, high-energy neutrons will cause simultaneous displacement damage and inert gas generation (through transmutation reactions) in the structural material of the first wall,
Dual-beam simulation techniques reproduce the simultaneous displacement damage and gas production in a relatively simple, inexpensive and rapid way.

§ 2. EXPERIMENTAL METHOD

The austenitic alloy used in this study was a ternary alloy of iron, nickel and chromium with a nominal composition 15% Cr, 15% Ni and estimated impurity levels of 0.006% C, 0.01% P, 0.001% Si and 0.04% Mn. Specimens in the form of 3 mm discs were punched from cold rolled sheet (0.2 mm thick) and vacuum annealed to produce a grain size of ~6 µm. The discs were then jet polished using 5% perchloric acid at −50°C to produce thin foils suitable for transmission electron microscopy.

The pre-thinned foils were then irradiated in the dual beam apparatus at A.E.R.E. Harwell (Evans, Faill and Goode 1971). Displacement damage was introduced by bombarding with 380 keV Cr⁺ ions, which are essentially self-ions. Simultaneous bombardment with 40 keV He⁺ ions was achieved using a second accelerator. The results reported here were obtained from a specimen irradiated at 600°C to a nominal dose of $2 \times 10^{14}$ Cr⁺ ions cm⁻² and $1 \times 10^{14}$ He⁺ ion cm⁻². The resultant displacement damage distribution and range curve (fig. 1) was calculated by a version of the E-DEP-1 computer code of Manning and Mueller (1974) modified by Matthews (1978). The peak damage level was ~0.5 d.p.a. and the damage rate was $4 \times 10^{-3}$ d.p.a. s⁻¹.

Irradiated specimens were examined using a JEOL-200CX microscope in normal transmission mode at an accelerating voltage of 200 kV. When examining dislocation loops at twin boundaries the ‘common g’ technique was

![Fig. 1](image)

Calculated displacement damage (——) and deposited ion concentration (---) for 380 keV Cr⁺ ions in the austenitic alloy.
Dislocation loops in ion-irradiated austenitic alloy used (Pond 1982). Here, reflecting planes which were common to both twin and matrix were chosen so the diffraction vector was identical on both sides of the twin interface. This is relatively simple in the twin case where a number of sets of planes are common to both twin and matrix.

§ 3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Analysis of the nature of the dislocation loops

Analysis of the Burgers vector of the dislocation loops was used to determine their interstitial/vacancy nature. This section describes this determination both for dislocation loops in the matrix and for those at coherent twin boundaries. Dislocation loops in the matrix were found to be typically 20-30 nm in diameter. These loops were imaged in two beam conditions using beam directions close to the [001] pole and the [102] pole of the matrix. A variety of diffracting vectors were used of the 200 and 220 types. The loops were found to lie on all four sets of {111} planes. Their Burgers vectors were found to be \( \frac{a}{3}[111], \frac{a}{3}[111], \frac{a}{3}[111] \) and \( \frac{a}{3}[111] \) and the loops were determined to be interstitial in nature using the inside/outside contrast method referred to in more detail below for loops at interfaces. The dislocation loops in the matrix were therefore faulted with an extrinsic stacking fault bounded by a dislocation of Burgers vector type \( \frac{a}{3}[111] \).

Fig. 2

131 dark-field micrograph with \( \Delta g \sim 0.03 \text{ nm}^{-1} \) showing triangular (T) and three-lobed (L) loops at a coherent twin boundary.
Dislocation loops at coherent twin interfaces were found to be adjacent to the twin plane and were not circular but exhibited three-fold symmetry. These loops were observed after dual-beam irradiations and also after irradiations using Cr+ ions alone. Small loops appeared approximately triangular as has been reported in copper by King and Smith (1980b) but larger loops had three lobes extending along the (112) directions of the twin plane (fig. 2). Figure 3 shows schematically the crystallography and shape of these loops. A Burgers vector determination was made more complex by the presence of the twin interface. This necessitated the use of the 'common g' technique where reflecting planes common to both twin and matrix were chosen. The technique ensured that any contrast effects due to the interface, such as fringes, were avoided. The twin plane was found to be a (111) plane using the matrix indexing system.

![Fig. 3](image)

The crystallography of (a) triangular and (b) three-lobed loops in the twin plane.

In order to achieve low values of $g \cdot b$ the chosen common diffraction vectors were 220 types, which are parallel to the twin plane, and 311 type, which are not. Imaging with the three 220 $g$ vectors which lie in the (111) plane resulted in no contrast from the loops (fig. 4). It is therefore apparent that the Burgers vector of the dislocation loops must be normal to the twin plane, that is $b = \pm a/3[111]$. The sign of the Burgers vector defines the vacancy or interstitial nature of the loops and can be determined by the change in inside/outside contrast of the dislocation image with sign of the diffraction vector (Mazey et al. 1962). This analysis has been made employing $g = \pm 311$ and $g = \pm 131$. The Burgers vector was found to be $b = a/3[111]$, and the loops were shown to be interstitial in nature (Mazey et al. 1962, Maher and Eyre 1971). We conclude that the three lobed loops found at coherent twin interfaces are interstitial loops with Burgers vector $a/3(111)$. This observation is consistent with the presence of similar interstitial dislocation loops in the matrix adjacent to the twins. Furthermore, matrix loops with the same Burgers vector as those at the twin interface show similar contrast effects with changes in diffraction vector.
Dislocation loops in ion-irradiated austenitic alloy

Fig. 4

A two-beam bright-field micrograph (g=220) of the same boundary as shown in fig. 2. The three-lobed loops are invisible. The intersection of the twin boundary with the foil surface is indicated by the arrows.

A model of an interstitial loop at a coherent twin interface is shown in fig. 5. The twin plane is indicated by a subscript T. The extra plane of interstitial atoms forming the dislocation loop is indicated by a subscript L. The model shows that the twin plane is effectively stepped up two (111) planes, but there is no extrinsic fault as would be the case in the matrix. Loops at the twin interface retain their \( a/3 \langle 111 \rangle \) Burgers vector and this is consistent with the observation of faulted loops in the matrix where the dissociation which would remove the fault has not occurred. The driving force for this reaction in matrix loops arises solely from the removal of stacking fault. The unfaulting mechanism, outlined earlier, occurs by the passage of two Shockley partial dislocations, one above and one below the extra atomic plane.

This mechanism is modified for \( a/3 \langle 111 \rangle \) loops at twin interfaces as shown by fig. 5. Now the passage of one Shockley partial dislocation merely moves the reflection twin plane down, reducing the step height to one (111) plane. An \( a/2 \langle 110 \rangle \) dislocation remains whose Burgers vector is out of the plane of the diagram. Thus dissociation of a loop at a twin interface requires the passage of only one Shockley partial dislocation and also results in a reduction in the step height of the twin interface. King and Smith (1980 a) suggest that the energy of a step at an interface is directly proportional to its height, so a driving force for dissociation of these loops could arise from the reduction in step height.
It is difficult to conclude whether the driving force for dissociation is greater for matrix loops than for loops at twins because little is known of the magnitude of interfacial step energies. However, we can conclude that nucleation of the dissociation reaction is easier in the twin case where only one Shockley partial dislocation is needed. Since neither the matrix loops nor the loops at coherent twin interfaces dissociate under the experimental conditions used, we cannot make any further deductions about the relative magnitudes of the various energies.

The stacking fault energy is known to change with additions of chromium to austenitic alloys (Silleck, Rookes and Barford 1966) and we have therefore considered the possible effects of implanting chromium ions. Figure 1 shows that the implanted chromium ion concentration exceeds 200 p.p.m. in a region 90–140 nm deep. These ions will come to rest in the visible regions of a thin film TEM specimen. However, since half of the atoms in the specimen are displaced from their atomic sites (0.5 d.p.a.) we anticipate a large mixing effect of matrix atoms and implanted ions. The observed interstitial clusters should be composed of iron, nickel and chromium atoms. The local chromium atom concentration at interstitial clusters will not be enhanced significantly. Any local alteration of the stacking fault energy will therefore be minimal and is unlikely to effect the unfaulting behaviour of loops.

3.2. Interstitial atom–twin interface interaction

Figure 6 clearly shows the presence of a 100 nm zone denuded of loops on both sides of the twin interface. This is direct evidence for a positive interaction between interstitials and the twin interface because diffusing interstitials
Dislocation loops in ion-irradiated austenitic alloy

Fig. 6

A bright-field micrograph showing the zone denuded of loops on both sides of a coherent twin interface.

come to rest preferentially at the boundary. This results in a local reduction of the interstitial concentration to a level below the super-saturation necessary for loop nucleation. This observation is in contrast to the vacancy case where coherent twin interfaces tend to be inefficient sinks for vacancies (Siegel, Chang and Balluffi 1980). Furthermore, in gas-bubble nucleation experiments, coherent twins have been found not to act as preferential nucleation sites (Braski, Schroeder and Ullmaier 1979), possibly due to the inability of such boundaries to trap the vacancies which are essential to bubble nucleation. The interstitial concentration in our experiment is particularly high because implanted ions come to rest in the region of interest (fig. 1). This is in addition to any interstitial concentration created by the displacement damage. Consequently, the driving force for interstitial clustering will be high. In the vacancy case, the sink efficiency of coherent twin interfaces is dependent on the vacancy supersaturation. We might therefore also expect coherent twin interfaces to behave as efficient interstitial sinks because of the high interstitial concentration. This would explain the nucleation of loops at the twin boundary despite the apparent absence of any other driving forces which would encourage the precipitation of interstitials. We must therefore deduce that there is a substantial positive interaction between an interstitial and the coherent twin boundary. Although no interaction would be predicted from considering
nearest-neighbour interactions, since to this approximation the twin boundary has the same stacking as the matrix, it is clearly necessary to take second-nearest neighbour interactions into account even to explain the stability of a twin. It is not surprising, therefore, that a point defect such as an interstitial, which has a large strain field, should experience an appreciable binding to the twin by perturbing second-nearest neighbour stacking.

This analysis is consistent with the conclusion of King and Smith (1980 b) that an interface may 'adsorb' a point defect which then travels within (or parallel to) the interface until it encounters a sink. The substantial binding energy which we deduce to exist between an interstitial and the twin boundary may be accompanied by a relatively low energy of interstitial migration within the boundary. A 'bound' interstitial need not be immobile.

3.3. The shape of loops in the twin boundary

All the interstitial loops found on twin boundaries in this work showed a three-fold axis of symmetry perpendicular to the twin plane. This symmetry is inherent in the coherent twin structure of an f.c.c. crystal, but this does not explain the three-lobed nature of the larger loops in which the dislocation line length is almost twice that which is strictly necessary to bound the same number of interstitials in a circular loop.

Three-fold symmetry has been observed in dislocation loops of both interstitial and vacancy type when they form as double loops within an outer faulted loop in several f.c.c. materials (Yoshida and Shimomura 1963, Tunstall and Goodhew 1966, Edington and Smallman 1965, Mazey and Barnes 1967).

The hexagonal shape of matrix faulted loops is best interpreted in terms of the formation and mobility of jogs along <110> directions (Yoshida, Kiritani and Shimomura 1963), although explanations in terms of the dissociation of the Frank partial into a stair-rod dislocation and a Shockley partial on an intersecting {111} plane have been proposed (Tunstall and Goodhew 1966). The dissociation argument has frequently been propounded for both triangular and hexagonal loops (see, for example, King and Smith 1980 b, Junqua and Grillhé 1980) but remains unconvincing because of the generally curved nature of the sides of the triangle (Tunstall and Goodhew 1966, Mazey and Barnes 1967). Similarly, in our observations the three-lobed loops exhibit virtually no linear segments and a mechanism involving dissociation onto another (111) seems improbable. It seems more likely that jog nucleation or mobility controls the shape.

Irregular dislocation loops, especially in the form of rosettes, have been reported in a number of materials (Sumida, Kiritani and Fujita 1975, Junqua and Grillhé 1980, Williams 1979, Shaw, Ralph and Stobbs 1981). A detailed analysis by Junqua and Grillhé (1980) has shown that a circular loop is unstable with respect to a dendritic (or rosette) loop if the ratio of pipe diffusion coefficient, \( D_p \), along the dislocation line to the bulk diffusion coefficient, \( D \), in the neighbourhood of the loop is sufficiently small. For a loop at an interface the appropriate value of \( D \) is usually that for diffusion within the interface, since this will in general be more rapid than in the bulk. There are a number of experimental situations in which the ratio \( D_p/D \) may be small. During electron irradiation in the HVEM, \( D \) in the lattice will be high, and Williams (1979) has observed rosette loops in grain interiors. At antiphase boundaries \( D \) may be
high and again rosette loops have been reported at this type of interface by Junqua and Grilhé (1980). In our case we can expect $D$ in the twin interface to be moderately high and in addition $D_\parallel$ may be depressed because of the effect of helium trapped at dislocation cores. This analysis is supported by our observation that rosette loops in the matrix of our material only occur when He$^+$ irradiation is used, and are not seen after implantation by Cr$^+$ alone.

It is now possible to explain the three-lobed shape of loops at coherent twin interfaces. In addition to the low value of $D_\parallel/D$ at such boundaries it is very likely that point defect migration in the boundary plane is anisotropic, with maxima in three symmetry-related directions. This effect will provide an extra driving force for the growth of a circular or triangular loop into the three-lobed shape which we observe. This is equivalent to replacing $D$ in the analysis of Junqua and Grilhé (1980) by an anisotropic planar diffusion coefficient of the form

$$D^* = D_\parallel(1 + \cos 3\theta),$$

where $D_\parallel$ is the average isotropic diffusion coefficient.

Once a three-lobed loop has formed, additional factors may act to stabilize it. Since each lobe is effectively a small dislocation dipole, it is easy to imagine that the three-lobed shape could be stabilized by the attractive interaction between the equal, but oppositely-directed dislocations on each side of the lobe (fig. 3). This option is not easily available to the inner triangle of a double loop because of the proximity of the outer hexagon and the directional nature of the vacancy flux to the centre of the defect (Bacon and Bullough 1968).

The above explanation for the shape of three-lobed loops essentially involves a kinetic argument based on diffusion and the mobility of jogs, followed by a stabilizing of the resultant shape by dipole forces. Any alternative explanation in terms of an equilibrium shape would need to invoke a large anisotropy of either (or both) dislocation line energy or twin boundary step energy. There is no evidence at present that either of these effects would be large enough to account for the presence of twice as much bounding dislocation as strictly necessary.

§ 4. Conclusions

(i) Irradiation-induced interstitials can cluster as dislocation loops at coherent twin boundaries in austenitic steel.

(ii) Such loops grow into a three-lobed shape, because the presence of helium reduces pipe diffusion along the bounding dislocation.

(iii) The presence of such loops, together with a loop-denuded zone on both sides of the boundary implies that there must be a positive interaction between an interstitial and the coherent twin.

Acknowledgments

The authors would like to thank SERC and U.K.A.E.A. Culham and Harwell Laboratories for support, and Professor A. G. Crocker for stimulating discussions.
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