HELIUM BUBBLES IN NIOBIUM AND
NIOBIUM - ZIRCONIUM ALLOYS

by

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The growth of Helium bubbles in Niobium and the binary solid-solution alloys Nb-0.3%Zr, Nb-1%Zr, and Nb-2.07%Zr, has been investigated in this work. Helium was introduced into thin sheets of these materials by sequential ion implantation, at room temperature, using the energies 220, 140, 100, and 50KeV. This produced a nearly uniform concentration of $5 \times 10^{26}$ He/m$^3$ (1 at.%) throughout a region 400 nm in depth. Subsequently each sample was annealed under vacuum for times up to 100 hours at temperatures between 850 and 1350°C, in order to precipitate and grow bubbles. The variation of the characteristic bubble size with annealing time was determined using quantitative transmission electron microscopy of suitably prepared samples. Bubbles in Nb and these Nb-Zr alloys are faceted $\{100\} / \{110\}$ polyhedra, or $\{100\}$ cubes, and they grow by a migration and coalescence mechanism. Surface diffusion limits bubble mobility in Nb at 950°C, but at 1050 and 1250°C the controlling kinetics are observed to change from surface diffusion to ledge nucleation. The ledge energy, $\epsilon$, is $1.5 \times 10^{-11}$ J/m at 1050°C, and $1.4 \times 10^{-11}$ J/m at 1250°C.

Bubble mobility in the Nb-Zr alloys is always ledge nucleation limited, and edge energies of $6.3 \times 10^{-11}$ J/m, $1.1 \times 10^{-10}$ J/m, and $4.3 \times 10^{-11}$ J/m, are deduced for Nb-0.3%Zr, Nb-1%Zr, and Nb-2.07%Zr, respectively, at 1050°C. A value of $1 \times 10^{-10}$ J/m was determined for Nb-1%Zr at 950°C. These values are greater than those deduced for Nb because the presence of Zirconium effectively cleanses bubble surfaces of interstitial impurities. Bubbles in Nb-0.3%Zr and Nb-1%Zr at 1050°C exhibit a breakaway/re-saturation phenomenon which, it is suggested, is caused by Zr-interstitial segregation effects. An ordering phenomenon that significantly influences bubble growth was observed in Nb-1%Zr at 1250°C. Finally, bubbles become over-pressurized during annealing, and this has an important bearing on the morphological changes of bubbles with time at temperature.
I would like to express my thanks to the many people who have discussed, and commented on, various aspects of the work presented in this thesis. I am indebted to Professor K.G. Stephens for making available the facilities of the Ion-Implantation Laboratory in the Department of Electrical and Electronic Engineering, and to the staff of this laboratory - particularly John Mynard and Mike Chapman - for performing the implantations. I am grateful to the SRC for the award of a Studentship, and to Professor M.B. Waldron for the provision of laboratory facilities. Special thanks must go to Dawn, Andy, Gill, Paul, and Jenny - the technical staff of the Structural Studies Unit in the Department of Metallurgy and Materials Technology - for their encouragement at all times. Finally, I have great pleasure in acknowledging my supervisor, Dr. Peter Goodhew, as a source of inspiration, and for his continual support and encouragement throughout the course of this work.
".... to travel hopefully is a better thing than to arrive, and the true success is to labour."

El Dorado

(Edgar Allan Poe)
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INTRODUCTION

As the earth's conventional energy reserves diminish, the search for alternatives becomes increasingly important. Sir John Hill (chairman of U.K.A.E.A.) has outlined the future trends in atomic energy and concluded that nuclear fusion can offer unlimited energy with minimal environmental risk (1). However, the huge scientific and technological problems associated with controlled thermonuclear reactions dictate that commercial reactors will take many years to develop.

The major materials problems of the first-wall of the plasma containment vessel derive from radiation damage. The high energy neutron fluxes responsible for the damage cause mechanical property changes, transmutation reactions, and swelling due to voids and inert-gas bubbles. Light-ion implantations from the plasma also produce undesirable effects, particularly sputtering and blister formation. The choice of material for first-wall use is very much dependent on reactor design, neutron absorption cross-section, coolant compatibility, high temperature mechanical properties, and the influence of transmutation on these conditions throughout operation. Austenitic stainless-steels, Nickel alloys, and the refractory metals V, Nb, and Mo with their alloys, are the most likely wall materials - the relative advantages and disadvantages of each is summarized in a recent review by Ehrlich (2).

This project has investigated the growth of Helium bubbles in Nb and Nb-Zr alloys (containing up to 2% Zr) during isothermal UHV annealing at temperatures between 850° and 1250°C. The Nb-Zr system is interesting because Zirconium is the major transmutation product of Niobium, and furthermore, both Nb and Nb-1% Zr have featured in conceptual designs. Hence, the influence of Zr on bubble growth mechanism and controlling kinetics can be deduced from the pure metal and alloys under identical conditions. Helium is generated by transmutation under reactor conditions.
and precipitates as bubbles which contribute to swelling and cause embrittlement. For this study Helium has been injected into Nb and Nb-Zr alloys by ion implantation to a concentration of 1 at.%. This grossly exaggerates transmutation concentrations but enables a high bubble density to be produced during annealing so that growth kinetics can be studied by transmission electron microscopy after hours, rather than years, at possible operational temperatures. Ion-implantation techniques have limitations when simulating the dynamic radiation environment of the first-wall, but using this technique as a He source for this investigation has enabled the effect of Zr on He bubble growth in Nb to be determined.
1.1 INTRODUCTION

A variety of materials have been suggested for use in the first-wall structure of fusion reactors. These include stainless-steels, refractory metals and alloys, Graphite, Silicon Carbide, and related ceramics. This chapter briefly reviews the properties required of candidate materials, and the merits and disadvantages of refractory metals over more conventional metals. Particular emphasis is placed on one of the more subtle problems of all materials, namely the production of Helium gas by transmutation in the wall. Transmutation of Niobium by the fast-neutron flux from the plasma is given in detail because of the applicability to the present investigation.

1.2 PROPERTY REQUIREMENTS OF THE FIRST-WALL

The primary function of the first-wall is to separate the plasma from the blanket and coolant. To do this effectively, whilst retaining efficient power generation, requires fulfilment of certain conditions. These are summarized by Mills (3) as:

1. Low neutron absorption cross-section.
2. High strength to withstand the coolant pressure and forces generated by magnetic field-liquid metal interactions.
3. Good corrosion characteristics – particularly with liquid metals, and finally
4. High resistance to long term radiation damage to ensure a useful working life.

These conditions are equally applicable to both Tokamak and Laser-fusion devices. The importance of each condition is dependent on the engineering design criteria.
of the specific reactor in question. However, Frank and Booth (4) have indicated that the effect of high-energy neutron irradiation on fatigue stress limits has particular significance - especially in Laser devices.

First wall geometries will be complex in order to reduce the high thermal stresses imposed upon it. A cellular Molybdenum wall was proposed by Rose (5), whilst Fraas (6) suggested a Niobium wall with the geometry shown in Figure 1. In this case the coolant channels have a triangular cross-section but square sections are equally permissible without being detrimental to heat-transfer considerations.

VACUUM

![Diagram of a Niobium First-wall geometry](image)

Liquid Li...
First-wall coolant

LiF-BeF$_2$ + Be ...(The Blanket)

FIGURE 1: A Niobium First-wall geometry suggested by Fraas (6).

An example of a complex geometry wall in a conceptual design is provided by the UWMAK 11 feasibility study (7). In this case the structure is comprised of semi-circular, type 316 stainless steel tubes attached to thicker backing material. More complex arrangements exist, like - for example - the segmented $\text{Al}_2\text{O}_3$ - Nb-1%Zr wall/blanket proposed by Thomassen et. al. (8) and Krakowski et. al (9) for the Reference Theta-Pinch Reactor. However, regardless of complexity, the wall structure should be designed to be
replaceable because operation in a stringent radiation environment makes it unlikely that wall lifetimes will exceed that of the reactor.

1.3 **REFRACTORY METALS: ADVANTAGES AND DISADVANTAGES**

A number of excellent reviews are available concerning the merits and disadvantages of candidate materials—notably by Erhlich (2), Conn (10), and Kulcinski (11). No single material fulfills the conditions of section 1.2 sufficiently to be an obvious first choice. Type 316 stainless steel is the most popular choice for near-term experimental reactors because of its data base and industrial availability. It has for example, appeared in American Tokamak designs utilizing Helium or water coolants (12,13). Refractory metals on the other hand, are capable of higher operating temperatures which yields higher thermal and power efficiencies. Stainless steels are limited to 500°C with Lithium-based coolants, whereas Niobium and the other refractory metals can sustain 1000°C under identical conditions (14,15).

Metal-coolant compatibility is an important criterion in the final choice of material. Refractory metals are superior with liquid Lithium coolants but suffer from severe Oxygen contamination when Helium gas is used (this is especially true for Nb and V). Purification of the Helium to a level where Oxygen contents are a few parts per billion is not economically viable so these materials are not considered with gaseous coolants (15). Thermal stress is also an important criterion. Schivell and Grove (16) have determined the heat-fluxes necessary to make thermal stresses exceed a) the UTS, and b) the melting point, of 1cm thick plate of various materials. Tungsten and Graphite were found to be particularly resilient followed by Niobium and Molybdenum. The other metals investigated—Ti, Zr, and type 304 stainless-steel—were found to be markedly inferior.
The same trend has been summarized by Conn (10) in terms of a 'Thermal-stress parameter' as a function of operating temperature (up to 500°C). In this case the superiority of refractory metals over 316 stainless steel is readily apparent.

Material choice for future commercial reactors will be influenced by radiation damage considerations. Sputtering and surface 'exfoliation due to blistering' cause cooling of the plasma, while bulk damage leads to ductility loss, void swelling, and eventual loss of integrity. Das and Kaminsky (17) have investigated the blistering phenomenon caused by incident He ions in Vanadium and type 304 steel, as a function of radiation dose and temperature. They found the maximum erosion rate occurred at 450°C for the steel, but at higher temperatures for Vanadium. They concluded that an optimum wall temperature should be chosen to minimize exfoliation, and to this end suggested 900°C for Nb and V. These refractory metals can operate at high temperature with minimum exfoliation while steels are limited to 500°C and a maximum erosion regime.

Void swelling and ductility loss can also restrict first-wall life. Bloom et al. (18) have studied the importance of each in a 20% cold-worked 316 steel irradiated at various temperatures with fast neutrons. Below 300°C life in excess of 10 years - limited by swelling - was expected, whereas irradiation between 300°C and 600°C results in a 10 year maximum lifespan due to ductility loss. The peak swelling temperature of many fast-neutron irradiated metals is approximately 0.45 Tm - where Tm is the melting point (19). Refractory metals with their high melting points also exhibit low swelling. For example - Nb, Mo, and TZM irradiated at 900°C with Ni ions to 5 dpa yield peak swelling values of only 0.83%, 1.0%, and 0.43%, respectively (20). Similarly, irradiation of Nb between 795°C and 932°C using heavy ions, with damage levels in excess of 35 dpa, only yields swelling in the region of 2.3 - 3.8% (21). It has also been reported that fast-neutron irradiated V-20%Ti does not suffer from void-
swelling at all (22). It would appear, therefore, that refractory metals offer the useful combination of low swelling with high temperature operation.

Having briefly outlined refractory metal advantages, their disadvantages can be summarized as follows:

a) Availability and cost are perhaps their major disadvantage. Only a limited industrial capability for production and fabrication exists which makes these metals expensive compared to steels or Nickel alloys.

b) There are also still many aspects of behaviour which are not well understood. This, coupled with other problems like the questionable weldability of Mo and TZM (15), means that design engineers tend to favour better characterized materials.

In the long term however, refractory metals will undoubtedly find important application in fusion reactor technology.

1.4 THE TRANSMUTATION OF Nb TO Zr AND He

Over many years of irradiation the chemical composition of the first-wall will be changed by nuclear transmutation reactions. Such reactions also produce radioactive species which determine wall activity when the reactor is shut down. Assuming a 2 year operation at a neutron wall loading equivalent to 1.25 MW/m², the activity level of various metals as a function of time after shut-down is summarized by Figure 2 (11). The advantage of V-20%Ti is readily apparent whereas Nb-1%Zr and 316 stainless steel have much longer lived activity.

Two transmutation products which occur in all materials are Hydrogen and Helium, the latter having negligible solubility leading to bubble precipitation causing swelling and embrittlement (23). Gas production rates assuming 1 MW/m² loading are given in Table 1 (11). Niobium (with the lowest gas production rate) also transmutes to
Radioactivity of CTR Blankets After Shutdown

The activity levels of first-wall materials after reactor shut-down.

![Graph showing radioactivity levels of different materials over time after shutdown](image)

**Table 1:** Gas production rates by transmutation assuming a neutron wall-loading of 1 MW/m²

<table>
<thead>
<tr>
<th>Material</th>
<th>dpa/yr</th>
<th>He appm/yr</th>
<th>H appm/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAB(a)</td>
<td>17</td>
<td>410</td>
<td>790</td>
</tr>
<tr>
<td>316 ss</td>
<td>10</td>
<td>200</td>
<td>540</td>
</tr>
<tr>
<td>Nb</td>
<td>7</td>
<td>24</td>
<td>79</td>
</tr>
<tr>
<td>Mo</td>
<td>8</td>
<td>47</td>
<td>95</td>
</tr>
<tr>
<td>V</td>
<td>12</td>
<td>57</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>2700</td>
<td>Negligible</td>
</tr>
<tr>
<td>Be</td>
<td>-</td>
<td>2800</td>
<td>130 Tritium</td>
</tr>
</tbody>
</table>

(a) 5-10% Al₂O₃ in an Al matrix.
Zr, Mo, and Y - with Zr as the major product. Martin \cite{24} has summarized the decay schemes, half-lives $T$, and cross-sections $\sigma$ for 14.1 MeV neutrons, as:

$$\begin{align*}
\nu_1 \text{MeV} &\quad \sigma \text{mbar} \\
93\text{Nb} + n &\rightarrow 92\text{Nb} + 2n - 8.8 \text{MeV} \\
&\quad (\sigma = 1232 \text{mbar})
\end{align*}$$

\text{a) electron capture}

$$\begin{align*}
92\text{Nb} &\rightarrow 92\text{Zr} \\
&\quad T = 10.1 \text{days}
\end{align*}$$

The $\sigma$ value quoted above is taken from the more recent data of Hermsdorf et al. \cite{25} and Jeki and Kluge \cite{26}.

$$\begin{align*}
93\text{Nb} + n &\rightarrow 90\text{Y} + \alpha + 4.9 \text{MeV} \\
&\quad (\sigma = 9.3 \text{mbar})
\end{align*}$$

\text{b) $\beta^-$ capture}

$$\begin{align*}
90\text{Y} &\rightarrow 90\text{Zr} \\
&\quad T = 64.2 \text{hours}
\end{align*}$$

$$\begin{align*}
93\text{Nb} + n &\rightarrow 93\text{Zr} + p + 0.7 \text{MeV} \\
&\quad (\sigma = 22 \text{mbar})
\end{align*}$$

\text{c) $\beta^-$ decay}

$$\begin{align*}
93\text{Zr} &\rightarrow 93\text{Nb} \\
&\quad T = 9.5 \times 10^5 \text{years}
\end{align*}$$

$$\begin{align*}
93\text{Nb} + n &\rightarrow 89\text{Y} + n + \alpha - 2.0 \text{MeV}
\end{align*}$$

The production of Molybdenum follows a more complex route.
but is given by Steiner (27) as:

In the above decay scheme 'm' denotes an isomer, and I.T an isomeric transition.

Helium and Zirconium production rates are highly dependent on the neutron wall-loading. However, assuming 1 MW/m$^2$ Steiner (27) and Kopecki et al. (28, 29) have shown that an initially pure Nb wall will contain 1.2% Zr, 270 ppm He, and a maximum of 0.36% Mo, after 10 years operation. More significant concentrations would be produced at 5 MW/m$^2$ - for example, 5.5% Mo instead of 0.36% (27). Fortunately Zr forms a body-centred cubic solid-solution with concentrations up to 11% in Nb (30) which means that embrittling precipitation is unlikely to determine wall lifetimes at useful neutron loadings. Zirconium is also beneficial to a number of properties whilst retaining little effect on nuclear properties. Better high temperature mechanical strength is obtained without significant
reduction in ductility. For example, the yield stress of Nb rises from 68.9 MN/m² to 276.0 MN/m² at 1095°C when containing 10% Zr, at the expense of a ductility reduction from 40% to 30% (31). There is also evidence that Zr increases resistance to grain boundary attack in molten Alkali-halide environments. Distefano and Litman (32) have reported that Niobium grain boundaries are attacked by molten Li-salts at 1000°C whereas no attack was observed if small amounts of Zr were present, provided the Oxygen content was below 1000 ppm. The absence of boundary attack was attributed to the removal of segregated Oxygen by the Zr.

Although generally beneficial, Zr complicates the interpretation of more subtle effects like the growth mechanism, and controlling kinetics, of Helium bubbles. These bubbles are not only generated by transmutation but also by implantation (at energies up to 3.5 MeV) from the plasma. Bubbles produced by the latter phenomenon are close to the wall surface and play an important role in blister formation and subsequent exfoliation (33). Gas bubbles are therefore important to both bulk and surface properties in a reactor environment. The purpose of this thesis is to identify the parameters of importance to bubble growth in Nb, and to examine the effect of Zr on nucleation and growth during high temperature annealing.
CHAPTER 2  THE DIFFUSION AND TRAPPING OF HELIUM

2.1 INTRODUCTION

The original impetus for inert gas bubble nucleation studies derived from the swelling phenomenon in fission reactor fuel elements. In these materials Xe and Kr are produced rather than the lighter He which is generated in fusion reactor containment vessels. Helium bubbles nucleate as a consequence of gas atom - lattice defect interactions. The purpose of this chapter is to outline these interactions, and their role in bubble nucleation after ion implantation. Throughout the chapter gas atom - vacancy complexes are denoted by $\text{He}_nV_m$ where $n$ and $m$ are the number of He atoms and vacancies, respectively, in the cluster.

2.2 HELIUM-LATTICE DEFECT INTERACTIONS

During implantation, vacancies and vacancy - clusters are produced nearer to the surface than the final position of the Helium atoms. Hence, gas atoms at the end of the range reside interstitially unless their mobility is high enough for them to jump into the vacancies they have produced (34). A single vacancy can accomodate more than one gas atom and the subsequent trapping of extra He or vacancies by such a cluster can lead to bubble nucleation.

Early calculations by Rimmer and Cottrell (35) predicted that the large inert gas atoms Ar, Kr, and Xe, would reside substitutionally in a metal lattice whereas Helium would occupy interstitial sites. However, interstitial He was expected to become rapidly substitutional in metals containing high vacancy concentrations. Johnson et al. (36) have computed the volume changes of b.c.c. metal lattices
when He is in substitutional, or interstitial, positions. Their results are summarized in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Volume change in atomic-volume units (negative signs indicate contraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V</td>
</tr>
<tr>
<td>Substitutional</td>
<td>-0.18</td>
</tr>
<tr>
<td>Interstitial</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Table 2: Lattice expansion associated with substitutional and interstitial He in b.c.c. metals.

It can clearly be seen that substitutional He produces a slight lattice contraction in refractory metals (but an expansion in Fe), while occupation of interstitial sites causes expansion.

The formation energies of a Helium atom in a variety of sites have also been computed for V, Fe, Mo, Ta, and W, using a sophisticated lattice relaxation technique (37). These energies are high for interstitial positions but low for vacancy occupation - as illustrated by Table 3.

<table>
<thead>
<tr>
<th></th>
<th>Formation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V</td>
</tr>
<tr>
<td>Substitutional</td>
<td>1.65</td>
</tr>
<tr>
<td>Interstitial</td>
<td>4.61</td>
</tr>
</tbody>
</table>

Table 3: Formation energies for He in an interstitial and pre-existing vacancy, in b.c.c. metals (37).
Harrison et al. (38) have shown that octahedral interstices are the preferred sites in b.c.c. metals in the absence of vacancies. The same preference is also predicted for Aluminium and Magnesium (39). Recent work has explained this for the latter metals in terms of a strong Helium potential interacting with the metal conduction electrons such that the gas atom seeks out sites of low charge density (40). Experimental verification that Helium will readily jump into vacancies has been supplied by a number of researchers. Snead et al. (41) have employed positron annihilation to demonstrate the phenomenon in Al, and Johnson and Cost (42) have used diffractometry to measure lattice parameter changes in Nb after implantation and annealing. The latter authors observed a lattice parameter decrease 30 times greater than expected and attributed this to substitutional occupancy of the gas atoms. The magnitude of the effect, however, suggests that multiple He - vacancy clustering has occurred rather than simple gas atom occupation of substitutional sites (36).

The most valuable experimental work is that by Kornelsen (43, 44) on Tungsten. He found that only a small fraction of He was trapped in the metal after implantation of (100) and (110) single crystals at energies below 400 eV, whereas significant trapping occurred above 500 eV (43). He postulated that the trapping observed for ion energies greater than 500 eV was due to displacement damage in the metal. To prove this, Helium was injected at 250 eV (below the displacement threshold) and the thermal release spectrum obtained during 40°K/sec heating - all the implanted gas was released during heating (44). When the Tungsten was first damaged with 5 KeV Kr ions and then injected with 250 eV He, the gas release spectrum obtained under identical conditions showed peaks only at discrete temperatures. The Helium was clearly trapped in the vacancies produced by the preliminary heavy-ion bombardment, and only released from the traps to diffuse interstitially to the surface at particular temperatures related to the binding...
energy of He in the defect.

The nature of these defects, and their dissociation at discrete temperatures, was postulated to be:

a) \( \text{He}_V \rightarrow \text{He} + V \quad 1560°K \\
\)
b) \( \text{He}_2V \rightarrow \text{He} + \text{He}_V \quad 1220°K \\
\)
c) \( \text{He}_3V \rightarrow \text{He} + \text{He}_2V \quad 1120°K \\
\)
d) \( \text{He}_4V \rightarrow \text{He} + \text{He}_3V \quad 950°K \\
\)
e) \( \text{He}_2V_2 \rightarrow 2\text{He} + 2V \quad 1675°K \\
\)

Kornelsen's experiments, therefore, not only demonstrated rapid He interstitial diffusion, but also multiple occupancy of vacancies with He binding energies decreasing as the number of atoms supported by the vacancy increased (this is illustrated by a) to d) above). On the other hand, He trapped at di- or tri- vacancies was found to be more tightly bound than to single vacancies - for example, e) above.

Wilson and Bisson (45) reanalysed Kornelsen's work theoretically and found excellent agreement with the latter's results concerning the assignment of release peaks to particular defect dissociations. Their calculations also indicated that up to six He atoms in an octahedral configuration could be accommodated by a vacancy, and 30 might be supported by the vacancy strain field. Extensive calculations for f.c.c. Cu (46) have suggested that between 5 and 8 He atoms per vacancy is permissible with \( \text{He}_6V \) being the dominant complex after room temperature implantation (34'). Experimental energies for the dissociations a) and b) above, have also been deduced from gas release spectra from (110) Molybdenum single crystals (47). Values of 3.0 eV and 2.5 eV for a) and b) respectively, were obtained compared with 4.2 eV and 2.9 eV from theoretical calculations. However, the dissociation

\[ \text{He}_V \rightarrow \text{He} + mV \]

required 3.4 eV for \( m=2 \) or 3 suggesting high stability for single gas atoms in di- or tri-vacancies as one might intuitively expect. The
formation energies, and binding energies, of Helium in di- and tri-vacancies have been computed for Molybdenum by Fasteneau et al. (48). It was shown that single gas atoms were bound tightly to both defects, and that each He$V_2$ and He$V_3$ cluster could be considered as He$V.V$ and He$V.V_2$ pairs respectively (although V$_4$ to V$_6$ configurations cannot be treated in this manner).

Thermal gas release spectra have also been obtained from implanted Niobium single crystals (49) but no attempt has been made to quantify specific defect configurations or dissociations even though activation energies were inferred from peak positions. Roth et al. (50) however, have demonstrated qualitatively that vacancies are again the principal trapping sites in this material, by implanting $^3$He at temperatures up to 1000°C and monitoring gas release during subsequent annealing. For implantation temperatures below 400°C all the $^3$He coming to rest in the metal was trapped by the vacancy damage it produced, whereas implants above 500°C yielded low trapping probabilities due to vacancy annihilation by annealing processes. It is likely, therefore, that He-V complexes in Nb are of similar configurations to those already described for Tungsten and Molybdenum.

Having outlined the nature and complexity of He-V interactions in b.c.c. metals after implantation it is possible to describe the processes which lead to bubble nucleation. During post-implantation heat treatment a cluster may (51)

1) Lose a Helium atom,
2) Lose a vacancy,
3) Migrate as a single entity to a sink or free-surface, or
4) Combine with another cluster.

This introduces the concept that He-V clusters can be highly mobile. The relative magnitudes of the cluster migration, vacancy binding, and He detrapping energies indicate whether a cluster migrates before losing either a
vacancy or gas atom. This is best illustrated by the computations of Caspers et al. (52) for Tungsten—some of which are reproduced in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Formation energy (eV)</th>
<th>He binding energy (eV)</th>
<th>V binding energy (eV)</th>
<th>Cluster migration energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>5.91</td>
<td></td>
<td></td>
<td>0.29</td>
</tr>
<tr>
<td>V</td>
<td>3.35</td>
<td></td>
<td></td>
<td>1.40</td>
</tr>
<tr>
<td>HeV</td>
<td>4.48</td>
<td>5.07</td>
<td>-</td>
<td>5.07</td>
</tr>
<tr>
<td>He₂V</td>
<td>7.25</td>
<td>3.43</td>
<td>-</td>
<td>5.0</td>
</tr>
<tr>
<td>He₃V</td>
<td>10.43</td>
<td>3.02</td>
<td>-</td>
<td>5.0</td>
</tr>
<tr>
<td>He₄V</td>
<td>10.73</td>
<td>2.94</td>
<td>-</td>
<td>5.0</td>
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<tr>
<td>HeV₂</td>
<td>7.56</td>
<td>5.29</td>
<td>1.67</td>
<td>1.6</td>
</tr>
<tr>
<td>He₂V₂</td>
<td>8.49</td>
<td>5.27</td>
<td>3.51</td>
<td>3.7</td>
</tr>
<tr>
<td>HeV₃</td>
<td>10.21</td>
<td>5.47</td>
<td>2.1</td>
<td>1.4</td>
</tr>
<tr>
<td>He₂V₃</td>
<td>11.18</td>
<td>5.23</td>
<td>2.06</td>
<td>1.4</td>
</tr>
<tr>
<td>He₃V₃</td>
<td>12.42</td>
<td>5.24</td>
<td>2.68</td>
<td>2.7</td>
</tr>
</tbody>
</table>

NB. Divacancy data is for a first neighbour configuration.

**TABLE 4:** Activation energies for HeₙVₘ clusters in Tungsten. (summarized from Caspers et al. (52)).

With reference to Table 4 it can be seen that:

1) HeₙV (with n>1) will lose He between 2.9 and 3.43 eV before migrating at 5 eV.

2) HeV₂ will migrate at 1.6 eV before losing a vacancy at 1.67 eV, or He at 5.29 eV.

3) He₂V₂ will lose a vacancy at 3.51 eV rather than become mobile at 3.7 eV, or lose gas at 5.27 eV.

4) He₂V₃ will migrate at 1.4 eV before losing a vacancy at 2.06, or He at 5.23 eV.

He₂V₂ and He₃V₃ configurations in Tungsten are found to be effectively immobile which is in agreement with computations for the same clusters in Molybdenum (48). This has lead to
the general conclusion that $\text{He}_{nV_m}$ clusters with $n=m$ are among the most stable in metals.

Once a He atom has detrapped from a cluster it can diffuse rapidly through interstitial sites. Typical activation energies for migration are about 0.2 eV in b.c.c. metals (37) which is comparable with that of Hydrogen in Niobium (53). If the gas atom reaches a free surface it contributes to the release spectrum; similarly, a mobile complex will also contribute to release. However, the dynamic interaction of initially detrapped He with both mobile and immobile clusters, and interactions between mobile and immobile complexes themselves, leads to bubble nucleation when vacancies are plentiful. In summary, therefore, bubble nucleation in ion-implanted metals is brought about by the complex and dynamic interaction of Helium, vacancies, and migrating or stationary $\text{He}_{nV_m}$ clusters.

2.3 DISLOCATIONS AS TRAPPING SITES FOR HELIUM.

Bullough and Newman (54) have shown that there is a strong elastic interaction between impurities and edge dislocations which results in significantly increased solute concentrations, and precipitation along the dislocation line (55). Greenwood et al. (56) have suggested that a similar phenomenon involving inert gases could lead to heterogeneous bubble nucleation at the dislocation. In such a case, the binding energy $U$ of a gas atom to a dislocation a distance $R$ away, is given by (56):

$$U = \frac{4Gbr_a^3 \epsilon \sin \alpha}{R}$$

where $G$ is the shear modulus, $b$ the Burgers vector, $r_a$ the atomic radius, $\epsilon_m$ the misfit parameter ($\epsilon_m = (r_g - r_a)/r_a$ where $r_g$ is the gas atom radius), and $\alpha$ the angle between the slip plane and the direction of $R$. The resultant concentration of gas atoms around the dislocation, $C_d$, is then related to the average...
concentration \( C_0 \), by the expression:

\[
C_d = C_0 \exp \left( \frac{-\psi}{kT} \right)
\]

For Xe in Uranium, the ratio \( C_d/C_0 \) may be as high as \( \sim 10^5 \) according to estimates of Greenwood et al. (56).

The large inert gas atoms found in irradiated fissile material have a positive misfit parameter \( \varepsilon \) and are attracted to the tensile side of an edge dislocation (56). Helium on the other hand, has a negative \( \varepsilon \) and would be attracted to the compressive side (57). High densities of He bubbles on dislocations have been observed by Murray (58) in irradiated Al - 0.1% Li, and by Vela and Russell (59) in Cu. These observations were used as evidence that dislocations do act as preferential nucleation sites. However, this is not necessarily a correct conclusion because it is extremely difficult to unambiguously eliminate the possibility that bubbles have grown below the visibility limit of the technique used to observe them, and then intersected the dislocation.

The most recent work concerning He - dislocation interactions is by de Hosson et al. (60) who have used sophisticated computer techniques to calculate the interaction energy of a gas atom with a \( \frac{1}{2}[111] (110) \) edge dislocation in Mo and W. Their method involved calculating the atomic positions in the dislocation using interatomic potentials and anisotropic elasticity theory, followed by computation of the potential energy of a He atom in a variety of positions around the core. The detrapping energy for the He atom is:

\[
\text{HeD} \rightarrow \text{He} + \text{D}
\]

was reported as 1.95 eV for Mo, and 1.93 eV for W. These are much smaller than the binding energies of He to vacancies (47, 52) and indicate that dislocations are not necessarily strong traps for this gas atom. However, migration energies along the dislocation line were calculated to be only 0.3 - 0.4 eV.
indicates the ease of pipe diffusion. Subsequent trapping at kinks or jogs has not been analysed but is thought to lead to very high binding energies and perhaps bubble nucleation (51). Hence, although dislocations may be preferential nucleation sites for the larger inert gas atoms, more research is necessary before any rigorous conclusions can be drawn regarding Helium.

2.4 SOME ASPECTS OF GAS RELEASE

In section 2.2 it was stated that He and He-V defects play an integral role not only in bubble nucleation, but also gas release both during implantation and subsequent annealing. Interest in the release phenomenon derived from its importance in fission fuels (61). Recently, however, Helium release from non-fissile material has received widespread attention due to the emergence of fusion technology. B.c.c. metals have low activation energies for interstitial He migration - for example, 0.13 eV and 0.23 eV for V, and Mo (37) respectively - so rapid diffusion can occur at relatively low temperatures. During implantation the observed fractional release is dependent on temperature (and hence trapping probability) and also the total dose received.

Niobium implanted at a number of temperatures with 300 KeV He ions exhibits a critical dose (1.5 x 10^{18} He/cm^2) above which significantly increased gas re-emission occurs (62). One reason for this is that He - V configurations formed during implantation may be dose dependent. Biersack et al. (63) have investigated He release from Nb and Mo during post-implantation annealing, using a nuclear depth profiling technique. No diffusional broadening of profile curves was observed, only amplitude changes. These observations lead to the conclusion that He must diffuse rapidly and that substitutional de-trapping of He was the rate controlling factor in gas release at high temperatures. A similar conclusion has been reached by Bauer and Wilson (64) for release above 400°C in stainless-steels, Cu, Pd,
and a variety of b.c.c. metals. In the latter case the de-trapping energies were found to be between 3 and 5 eV.

The mathematics of gas release are well developed for both fissile material (61) and potential structural materials. The importance of the re-trapping phenomenon as the gas diffuses to the free surface has been recognized for many years and accounted for in various analyses. Early work by Kelly and Matzke (65) assumed constant temperature, and gas diffusion coefficient, with bubbles as the only permanent traps for diffusing gas. It was acknowledged, however, that 'weak' interactions between gas and lattice damage were also likely. Roodbergen et al. (55) have accounted for re-trapping in diffusion theory to produce a computer model to calculate desorption spectra. The application of this work to Tungsten has demonstrated that re-trapping can explain the tendency of desorption peak shift to higher temperatures in high dose - high damage experiments.

Gas release allowing for re-trapping during a linear, or more complex, temperature rise has been analysed by Carter and co-workers (67, 68). For a semi-infinite solid subjected to a heating function of the type

\[ \frac{1}{T} = \frac{1}{T_0} - bt \]

where \( T_0 \) is the initial temperature, \( b \) the heating rate constant, and \( t \) time, the concentration of gas in traps is given by (67):

\[ m(x,t) = \frac{1}{L^2 h^2} \int D C(x,t) \, dt \]

Here \( L \) is the mean intertrap distance in terms of \( h \) the interplanar spacing, and \( C(x,t) \) is the instantaneous concentration of freely diffusing gas atoms whose diffusion coefficient is \( D \). (The more usual heating function employed experimentally is \( T = T_0 + bt \) but the reciprocal relationship above is more amenable to theoretical analysis.)

Assuming that the gas is initially at a depth \( R \) below the surface, the total quantity trapped at depth \( x \) over all time (ie. \( t \rightarrow \infty \)) is given by two general equations:
$$m(x,\infty) = \frac{C_0 e^{-\frac{R}{L}}}{2L} \left[ \frac{x}{e^{R/L}} - \frac{x}{e^{R/L}} \right]$$ for $x > R$

$$m(x,\infty) = \frac{C_0 e^{-\frac{x}{L}}}{2L} \left[ \frac{R}{e^{R/L}} - e^{-\frac{R}{L}} \right]$$ for $x < R$

where $C_0$ is the initial gas atom concentration at depth $x$. These are identical results to those of Kelly and Matzke (65) for the constant temperature condition. In summary, therefore, it can be concluded that gas release and bubble nucleation are inter-related phenomena, both highly dependent on the nature of He - V interactions. De-trapping from vacancy clusters, and re-trapping during diffusion, are particularly important processes in both phenomena.
CHAPTER 3  HELIUM BUBBLE GROWTH MECHANISMS
IN MATERIALS

3.1 INTRODUCTION

Once nucleated He bubbles may grow by one of two general mechanisms:

a) The re-solution of gas from small bubbles and precipitation into larger ones in a manner analogous to Ostwald ripening of solid precipitates, or

b) By migration of the bubble as a whole, and coalescence on collision with other bubbles.

Few researchers have studied bubble growth kinetics in b.c.c. candidate first-wall materials but some investigations have been undertaken for other well-characterized metals and nuclear fuels. A review of the theoretical equations describing bubble growth during post-implantation annealing is presented in this chapter together with some relevant experimental investigations.

3.2 RE-SOLUTION

Inert gases are virtually insoluble in solid materials (35) and consequently readily precipitate as gas bubbles. Actual solid solubilities are difficult to quantify but some data is available for liquid systems. An illustrative selection of inert gas solubilities in liquid metals is given in Table 5. The data given in this table is summarized from a similar table published by Blackburn (57), and it clearly illustrates marked insolubility in the liquid phase. Brinkman and Johnston (69) however, have quoted work which apparently demonstrated the ability of \(^{85}\)Kr to dissolve in Cu, Ni, Al, and other metals, at pressures up to 2000 atmospheres, and temperatures as low as 400°C. If this was the case an Ostwald ripening type of growth mechanism cannot be ignored. The most extensive analysis of the re-solution of small bubbles in preference to larger ones, is presented by
<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>TEMPERATURE °C</th>
<th>SOLUBILITY atom fraction/atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr-Ag</td>
<td>1000</td>
<td>( \approx 10^{-11} )</td>
</tr>
<tr>
<td>Xe-Na</td>
<td>150</td>
<td>( 6 \times 10^{-6} )</td>
</tr>
<tr>
<td>Ar-Na</td>
<td>480</td>
<td>( 2.4 \times 10^{-9} )</td>
</tr>
<tr>
<td>He-Bi</td>
<td>500</td>
<td>( \approx 10^{-9} )</td>
</tr>
<tr>
<td>He-K</td>
<td>482-704</td>
<td>( 2.9 \times 10^{-6} - 8.4 \times 10^{-6} )</td>
</tr>
<tr>
<td>He-Li</td>
<td>649-871</td>
<td>( 5.0 \times 10^{-9} - 7.4 \times 10^{-9} )</td>
</tr>
</tbody>
</table>

**TABLE 5:** Inert gas solubilities in liquid metals (after Blackburn (57)).

Greenwood and Boltax (70). They have assumed that all the gas is contained within bubbles which are growing at constant temperature.

If a spherical bubble radius \( r_1 \) and pressure \( P_1 \) dissolves such that a neighbouring bubble grows from radius \( r_2 \) to \( r_3 \), with a pressure change from \( P_2 \) to \( P_3 \), then

\[
\frac{4}{3} \pi r_1^3 P_1 + \frac{4}{3} \pi r_2^3 P_2 = \frac{4}{3} \pi r_3^3 P_3
\]

if the number of gas atoms is conserved. At equilibrium the bubble gas pressure balances surface tension forces such that \( P_1 = 2Y/r_1 \) etc.

\[
r_1^2 + r_2^2 = r_3^2
\]

Thus the total surface area remains approximately constant throughout, and the driving force for growth derives from the reduction in gas pressure and hence gas free energy. This driving force differs radically from the reduction in surface energy per unit volume which leads to precipitate coarsening.

The equation describing the gas concentration \( c \) in the solid surrounding a bubble of sparingly soluble monatomic gas at pressure \( P \), has the form (71, 72):

\[
c = P \exp \frac{\Delta S}{k} \exp \frac{\Delta H}{kT}
\]

........... (3.1)
where $\Delta H$ is the heat of solution, $\Delta S$ the vibrational entropy change of the lattice, and $kT$ has its usual meaning. Substitution of $P=2\gamma/r$ into equation 3.1 clearly shows that small bubbles are surrounded by higher gas concentrations than larger ones. Therefore a concentration gradient exists between small and large bubbles. Greenwood (72) has shown that equation 3.1 is also valid for non-spherical bubbles. In general, therefore, for any bubble population, those of the mean size neither dissolve nor grow, while those smaller dissolve at rates increasing as their size decreases. The time required for a bubble to grow from radius $r_1$ to $r_2$ at temperature $T$ by a thermodynamically driven re-solution mechanism, is given by (70):

$$r_2^2 - r_1^2 \sim D_g t \exp - \frac{G}{kT} \quad \ldots \ldots \quad (3.2)$$

where $D_g$ is the gas diffusion coefficient, and $G$ the free energy of solution. Barnes and Nelson (73) have compared the re-solution and migration mechanisms for bubbles of various sizes in Cu at 1200$^\circ$K. Re-solution was concluded to be very unlikely.

Although He re-solution is unlikely during post implantation annealing evidence exists that intergranular bubbles of other sparingly soluble gases do coarsen in this manner. Wolfenden and Farrell (74) have simplified an early equation given by Greenwood and Boltax (70) to obtain:

$$d^3 \sim 18 D_g t \exp \frac{U - G}{kT} \quad \ldots \ldots \quad (3.3)$$

where $d$ is the boundary bubble's diameter, and $U$ the binding energy of the gas to the boundary. Greenwood (75) on the other hand, has derived a more complex equation for the time dependence of the bubble size during annealing. Both research groups have used their respective equations to demonstrate re-solution controlled growth of fluorine-containing pores in Tungsten wires used for electric light bulb filaments.

The most extensive research on re-solution, or gas diffusion controlled growth, has concerned nuclear fuels.
In these materials irradiation induced re-solution is a well-known phenomenon. Whapham (76) has suggested that the local, and rapid, heating caused by a passing fission fragment can lead to explosive disintegration of a bubble. Alternatively, Nelson (77) has proposed that the gas is re-dissolved by a sputtering process when an atomic projectile collides with the bubble. The resultant supersaturated solution of gas can precipitate during subsequent annealing to yield bubbles whose growth is controlled by gas atom diffusion in the matrix. This situation has been dealt with by Speight (78), Markworth (79, 80), and Cornell (81). Informative reviews on the specific subject of bubble behaviour in nuclear fuels are published by Dias and Merckx (82) and Urlander (61).

3.3 MIGRATION AND COALESCENCE

Inert gas bubble growth by migration and coalescence was first observed in Cu containing 0.1 atomic % He during pulse annealing in a transmission electron microscope (83). This phenomenon has since been reported in many other metallic systems. Bubble movement may be random - i.e. analogous to Brownian motion - or influenced by microstructural features, temperature gradients, or applied stress. Actual mobility can be characterized in a number of ways but usually in terms of a bubble diffusion coefficient, $D_b$. Greenwood and Speight (84) introduced the concept of $D_b$ using the random walk diffusion equation:

$$D_b = \frac{1}{6} \overline{q}_{b}^2$$

where $\overline{q}_{b}$ is the bubble jump frequency, and $q_{b}$ the jump distance. $D_b$ is related to the atomic processes causing migration via these parameters. Alternatively, characterization can be by RMS migration distance or velocity which are related to $D_b$ by the relevant diffusion equation and the Nernst-Einstein relationship.
Here $F$ is a driving force.

For a bubble to move a net flux of atoms from the leading to trailing surface is necessary. This transfer can be controlled by:

a) Surface diffusion around the bubble perimeter,

b) Volume diffusion through the matrix,

c) Transport through the gas in the bubble, or

d) Ledge nucleation phenomena at the surface.

If coalescence is rapid after collision these mechanisms control the growth rate.

### 3.3.1 Surface diffusion control

Barnes and Mazey (83) found the velocity of He bubbles in TEM pulse-annealed Cu could be described by:

$$ v = \frac{D_s}{8\pi kT} \left( \frac{a}{r} \right)^4 F \quad \ldots \ldots \ldots (3.5) $$

where $a$ is the lattice parameter, $r$ the radius, and $D_s$ the surface diffusion coefficient. Surface diffusion was considered to control bubble movement. Shewmon (85) predicted that surface diffusion would be the dominant control mechanism for bubbles smaller than 1μ, and he derived the following equation from first principles:

$$ v = \frac{\pi D_s \delta}{\pi r^4} F \quad \ldots \ldots \ldots (3.6) $$

where $\delta$ is the thickness of the high diffusivity surface layer, and $\pi$ is the atomic volume. These two equations predict velocity to be a strong function of size with large bubbles having lower mobilities than small ones. A comparison of equations 3.5 and 3.6 with the Nernst-Einstein relationship, equation 3.4 implies that $D_b v r^{-4}$. This radius dependence has been confirmed by Barnes
and Nelson (73), Nichols (86), and Kelly (87) who have derived the following equations respectively:

\[ D_b = \frac{2 \Omega^3}{\pi^2 r} \]  
\[ D_b = \frac{3a \Omega D}{2 \pi r^2} \]  
\[ D_b = \frac{3D_s}{2 \pi r} \]

The apparent omission of \( a \) (where \( a \) is the lattice parameter) in equation (3.9) is due to the particular model used in its derivation, and slight differences in the definition of \( D_b \). However, independent of the derivation method \( D_b \) is always proportional to \( r^{-4} \). Mikhlin and Chkuaseli (88) have produced an alternative equation which accounts for gas non-ideality in small \((r < 10 \text{ nm})\) bubbles, and the dependence of \( D_g \) on surface curvature. An exponential term is incorporated such that:

\[ D_b = \frac{3a^4 D_{so}}{2 \pi r^4} \exp\left(-\frac{2\Omega Y}{r\kappa T}\right) \]

where \( D_{so} \) is an experimental value of the surface diffusion coefficient.

In view of the work reported in this thesis the most useful equations relate bubble size to post-implantation annealing temperature and time. These relationships have evolved from Chandrasekhar's (89) treatment of colloid coagulation based on the Brownian motion theory of Von Smoluchowski (90). The number of collisions \( \Delta F_{ij} \) between spherical bubbles of radii \( r_i \) and \( r_j \) in time \( \Delta t \) can be described by:

\[ \Delta F_{ij} = 4\pi D_{ij} R_{ij} C_i C_j \left[ 1 + \frac{R_{ij}}{(\pi D_{ij} \Delta t)^{1/2}} \right] \Delta t \] 

\( D_{ij} \) is the sum of the bubble diffusion coefficients \( D_i \) and \( D_j \), \( R_{ij} \) is the interaction distance \( r_i + r_j \), and \( C_i, C_j \) are the number of bubbles of size \( r_i \) and \( r_j \) per unit volume.

Any kinetic control mechanism can be considered by substituting the appropriate equations for \( D_i \) and \( D_j \).
Gruber (91) has used the first term only of equation (3.10) - a valid simplification if the distance travelled by two bubbles relative to each other is large compared to the sum of their radii - to calculate size distribution changes for surface diffusion control, as a function of time. If the gas in bubbles obeys the ideal gas laws, and the initial bubble size is negligible, the mean radius as a function of time at temperature is given by (91):

$$r \sim 1.30 \left( \frac{mkT \alpha h D_s t}{\gamma} \right)^{1/5} \ldots \ldots . (3.11)$$

Baroody (92) has used similar analytical computer techniques and found the same $t^{1/5}$ dependence. Both analyses confirm the time dependence of $r$ derived by Speight (93) using approximate "coalescence time" calculations. Gruber (94) has since modified his analysis to investigate the effect of including the second term in equation (3.10). After long times at temperature the time dependence is expected to change from $t^{1/5}$ to $t^{3/4}$.

Aitken et al. (95) have approximated the size distribution to a single value - the average - to investigate whether errors are introduced. Equation (3.11) was re-derived with a numerical coefficient of 1.35 instead of 1.30. Hence serious errors are not introduced when a bubble population is characterized by a single dimension. The same authors have also derived a growth equation for spherical gas bubbles deviating from ideality, and surface diffusion controlled (95). It is, however, complex and not reproduced here. Surface diffusion limited migration is reported for Helium bubbles in Cu (83) and Nb (96, 97), while Ruedl and Kelly (98) have attributed the same mechanism to Kr bubbles migrating in Pt. Kaletta (99) has observed He bubbles during blistering experiments with Vanadium and reported a migration and coalescence growth mode without specifying the controlling kinetics. Smidt and Pieper (100) on the other hand, tentatively assigned surface diffusion control to He bubbles in this material. They have acknowledged, however, that
their low experimental $D_b$ values could indicate a nucleation limited mechanism.

The equations reviewed above are derived for spherical bubbles whereas a $\{100\}$ cubic morphology is often observed in refractory metals (100,101). Growth equations and $D_b$ for this morphology are derived in Appendix I.

3.3.2 Volume diffusion control

Shewmon (85) has suggested that control mechanisms other than surface diffusion will only become important for bubble sizes greater than $1\mu$ or so. Bubbles of this size are not expected in fusion reactor structural metals, but are observed in fission fuel elements. For example, Barnes and Nelson (102) have predicted that fission bubbles in UC at $1750^\circ C$, migrating in a $1000^\circ C/cm$ temperature gradient, would be surface diffusion limited for $r<5\mu$ but volume diffusion controlled for larger sizes. The theoretical $D_b$ equations for this mechanism have again been derived by Barnes and Nelson (73), Nichols (86), and Kelly (87). Nichols (86) and Kelly (87) have given, respectively:

$$D_b = \frac{3\Omega D_v}{4\pi r^3} \quad \ldots \ldots (3.12)$$

$$D_b = \frac{3 D_v}{2\pi f r^3} \quad \ldots \ldots (3.13)$$

where $f$ is the correlation coefficient given by $D_v = f C_v D_v$. Here $C_v$ is the vacancy concentration, and $D_v$ the vacancy diffusion coefficient.

It should be noted that $D_b \propto r^{-3}$ regardless of the geometric model used for the derivation. Consequently bubble mobility again decreases as size increases.

Analysis of volume diffusion controlled random migration and coalescence for spherical bubbles during annealing after irradiation, yields $r \propto t^{\frac{1}{4}}$ regardless of whether equation (3.12) or (3.13) is used (95). A log (radius) vs log (time) plot should therefore have a slope of $0.25$ instead of
the 0.2 expected for a surface diffusion mechanism. Although a surface diffusion limited mechanism should be dominant for small bubbles \( r < 10 \text{ nm} \), volume diffusion cannot be neglected when highly alloyed materials are under investigation. Walker (103), for example, has studied He bubble growth in ion-implanted 20%Cr 25%Ni - Nb stabilized steel during anneals between 800\(^\circ\) and 900\(^\circ\)C. Volume diffusion of Cr was found to best explain bubble behaviour for radii greater than 5 nm. However, more work is necessary on these systems before any general conclusions can be drawn.

3.3.3 Vapour transport control

An evaporation-condensation mechanism, involving diffusion through the gas, should be unfavourable with respect to surface or volume diffusion in all materials except volatile halides (e.g. CaF\(_2\), NaCl, KCl etc.) and perhaps metals with volatile oxides (87). A survey of the available literature reveals that a) this statement is generally correct, and b) the bubble sizes at which vapour transport could dominate are vastly in excess of those normally observed in irradiated metals. For example, vapour transport should only become important for fission gas bubbles migrating in 1000\(^\circ\)C/cm temperature gradients in UO\(_2\) and UC at 1750\(^\circ\)C, for \( r \sim 800 \text{ nm} \) and \( r \sim 0.1 \text{ mm} \), respectively (102). Ashbee (104), however, has assumed vapour transport control for much smaller migrating bubbles in UO\(_2\) subjected to TEM pulse annealing.

Experiments performed by Buescher and Meyer (105) on He implanted, single-crystal UO\(_2\), subjected to a measured 1000\(^\circ\)C/cm temperature gradient, again reveal that vapour transport is unimportant until large bubble sizes. A step-nucleation limited mechanism was assigned to small sizes \( r < 10 \text{ nm} \), while for \( 10 \text{ nm} < r < 1 \mu \) a surface diffusion mechanism modified by gas atom interference was proposed. Beyond 1\( \mu \), an evaporation-condensation mechanism was found
to be dominant. The migration of gas-filled pores in alkali halides and other inorganic material is also vapour transport limited. Air bubbles of complex morphology in NH\textsubscript{4}Cl (106), and He filled pores (r \approx 165 \mu m) in KCl (107), are both controlled by this mechanism when subjected to a thermal gradient driving force. Similarly, Antony and Sigsbee (108) have proposed the evaporation-condensation phenomenon to explain the mobility of pores (r \geq 10 \mu m) in Camphor.

The velocity of randomly migrating, vapour transport limited, inert gas bubbles is given by Barnes and Nelson (73) as:

\[
\nu = \frac{2}{2\pi r^2} \cdot \frac{D_g P_T Q}{(kT)^2} \cdot F \tag{3.14}
\]

P\textsubscript{T} is the vapour pressure of the solid, Q the heat of evaporation, and D\textsubscript{g} the diffusion coefficient of metal atoms in the gas. Equation (3.14) once more predicts a reduction in mobility as bubbles become larger, and a comparison with equation (3.4) indicates D\textsubscript{b} \propto D\textsubscript{g}/r^{-3}. More precise equations for D\textsubscript{b} are derived by Kelly (87) and Nichols (86) respectively, as:

\[
D_b = \frac{3D_g C_g \lambda^2}{4 \pi r^3} \tag{3.15}
\]

\[
D_b = \frac{3D_g P_T a_v^2}{(4 \pi kT r^3)} \tag{3.16}
\]

Here \lambda is the interplanar spacing, C\textsubscript{g} the concentration of metal atoms in the gas (ie. related to P\textsubscript{T}), and a\textsubscript{v} a measure of gas deviation from ideality. Both equations verify the D\textsubscript{g}/r\textsuperscript{-3} dependence deduced from equation (3.14).

Analysis for the time dependence of bubble size during post-implantation annealing assuming D\textsubscript{b} \propto r\textsuperscript{-3}
reveals \( r \propto t^{\frac{1}{6}} \) - the same dependence as a volume diffusion mechanism (96). This result is valid only if \( D_0 \) is independent of \( r \). However, a number of authors (73, 87, 105, 109) realised that \( D_0 \) could be described using the kinetic theory of gases such that:

\[
D_0 = \frac{2kT}{3P\sigma} \sqrt{\frac{2kT}{\pi}} \left[ \frac{1}{M_1} + \frac{1}{M_2} \right]
\]

where \( M_1 \) and \( M_2 \) are the molecular masses of the two constituents of the gas - ie. metal vapour and Helium, \( \sigma \) is the collision cross-section, and \( P \) the total pressure in the bubble. If the pressure \( P \) balances the surface tension forces such that \( P = 2\gamma/r \), then \( D_0 \propto r \) and \( D_b \propto r^{-2} \) not \( r^{-3} \). Subsequent analysis for the time dependence of bubble size during annealing would yield \( r \propto t^{\frac{1}{3}} \).

### 3.3.4 Facet nucleation-limited control

Experimental work on a variety of materials has revealed unsatisfactory agreement with the diffusion controlled migration and coalescence models of sections 3.3.1 to 3.3.3. For example, Willertz and Shewmon (110) have found bubble mobilities in Cu and Au to be an order of magnitude, and \( 10^4 \) to \( 10^5 \) times slower, respectively, than predicted by surface diffusion models. In order to explain such discrepancies it is necessary to consider bubble shapes in more detail. Shape is essentially governed by the minimum surface energy per unit volume but because surface energy is often anisotropic bubbles are frequently faceted on low index planes (see for example Refs. 100 and 101). Nelson et al. (111) have specified the shape determining parameters and show that at thermal equilibrium bubbles...
should indeed be faceted. Therefore in systems where faceting is observed an alternative limiting mechanism is possible, namely, the nucleation of ledges on the atomically smooth surface rather than the surface diffusion of individual atoms.

An analogous problem exists in catalysis where the migration and coalescence of faceted particles on substrates is of interest. This problem has been dealt with in terms of a step nucleation mechanism by Wynblatt and Gjostein (112), while Willertz and Shewmon (110) have applied the analysis to bubble migration. The probability of nucleating an atomic ledge in the shape of a 'pillbox' at the centre of a circular facet is:

\[ \text{Probability} = \exp \left( - \frac{2\pi gr\epsilon}{kT} \right) \]

where \( g \) is a geometrical factor, \( r \) the bubble radius, and \( \epsilon \) the edge energy of the step produced. The nucleation frequency of critical size – i.e. stable – pillboxes can be estimated from ad-atom/pillbox collision rates, and used to deduce \( D_b \). In this case \( D_b \) is given by:

\[ D_b = \frac{D_s r}{\alpha_s} \exp \left( - \frac{2\pi gr\epsilon}{kT} \right) \quad \ldots \ldots (3.18) \]

where \( \alpha_s \) is the ad-atom jump distance on the surface.

Chen and Cost (113) have also invoked a step nucleation model to explain the low growth rate of polyhedral He bubbles in Al during post-irradiation annealing. Two models were proposed to derive \( D_b \) relationships based on extremes of the critical nucleus concept.

a) The emitting - ledge model

The facet is assumed to be flat and circular, and the critical nucleus size is considered to be a ledge which is a facet diameter. Furthermore, emptying
of the facet is taken as rate controlling. The model also
differs from that of Willertz and Shewmon (110) in so much as
nucleation can occur anywhere on the facet instead of only
at its centre. Within these assumptions \( D_b \) is given by:

\[
D_b = \frac{h \pi \delta D s^2}{3 a^2} \exp \left( -\frac{2g \xi r}{kT} \right) \quad \ldots (3.19)
\]

b) The two-pillbox model

This model considers the total edge energy change when atoms are exchanged between adjacent smooth, circular facets. Pillboxes are retained as critical nuclei but nucleation is again allowed anywhere on the surface. If the free-energy change is given approximately by the total energy change of ledges, and entropy terms are ignored, \( D_b \) is given by:

\[
D_b = \frac{0.79g^3 \delta s^3}{d^2 b} \exp \left( -\frac{2\sqrt{2} \pi \delta \epsilon r}{kT} \right) \quad \ldots (3.20)
\]

The most important differences between equations (3.19), (3.20), and (3.18) are found in the exponential term which dominates each relationship. The exponential terms of equations (3.19) and (3.20) are \( \pi \) lower and \( 2\sqrt{2} \) larger, respectively, than that of equation (3.18). This is a direct consequence of the ledge geometries considered in each model.

Results consistent with nucleation limited kinetics are reported by Pati and Maiya (114), Coleman (115), and Shiraishi et al. (116), for bubbles in Cu, Au, and Al respectively. Furthermore, Buescher and Meyer (105) and Baker (117) have both invoked facet-nucleation to explain the immobility of small (\( r < 10 \text{ nm} \)) bubbles in UO\(_2\). Beéré (118) has applied the nucleation limited concepts to bubbles in Cu intersected by dislocations. Surface steps introduced by the dislocation reduce the critical ledge nucleation energy which leads to a higher mobility along the dislocation line than in the perfect lattice. Beéré and
Reynolds (119) have also shown that certain bubble faces preferentially emit vacancies. In view of this they have derived face velocity equations in terms of both step nucleation and surface diffusion. Their analysis has been extended by Tyler and Goodhew (120) to derive a ledge nucleation limited \( D_b \) for bubbles of \( \{100\} \) cubic morphology. For a bubble having a cube dimension \( c \), \( D_b \) is given by:

\[
D_b = \frac{D_s \bar{n} c}{6a} \exp \left( -\frac{n c \ell}{2kT} \right) \quad \ldots \ldots (3.21)
\]

This equation becomes more complex if 'brick-shaped' \( \{100\} \) bubbles are considered rather than cubes (120).

Few experimentalists have quantitatively studied He bubble growth in b.c.c. metals so evidence for particular kinetic mechanisms is sparse. Johnson and Cost (121) however, qualitatively observed a terminal bubble size in implanted and annealed Nb, and Smidt and Pieper (100) have not discounted the possibility of a nucleation limited mechanism in V. More recently it has been shown that He bubbles growing at 1050°C in Nb are at some stage facet-nucleation limited, while those in Nb - 1%Zr are always nucleation limited under identical conditions (120).

The relationship between bubble radius \( r \) and post-irradiation annealing time \( t \) is not clarified in the literature. Shiraishi et al. (116) have used an equation derived from equation (3.18) to predict bubble growth in Al, whereas Chen and Cost (113) found \( r \propto t^{1/2} \) at short times but rapidly becoming \( \sim t^{0.05} \) as time proceeded. Helium bubbles growing in irradiated Cu - 0.04% B by migration and coalescence indicate \( r \propto t^{0.07} \) and although controlling kinetics were not inferred faceted bubbles were observed (122).

Similarly, faceted bubbles in Al - 0.3%Li have shown \( r \propto t^{0.05} \) during annealing at 200°C (123). These growth and shape observations are consistent with nucleation limited migration. A more detailed discussion of the important parameters in a
growth equation derived from equation (3.21) is presented in Appendix II. The equation derived has been applied with some success to bubble growth in Nb and its alloys.

3.3.5 Coalescence

Descriptions of the coalescence phenomenon are given by Eyre and Bullough (124), and in more detail by Nichols (86). Following Nichols (86) analysis we can sub-divide coalescence into two stages: 1) actual coalescence at constant volume when two bubbles collide, and 2) volume adjustment by vacancy collection to re-establish equilibrium. The free energy change for the whole process \( \Delta G_t \) equals the sum of the changes in 1) and 2), \( \Delta G_c \) and \( \Delta G_{\text{vol}} \) respectively.

1) Coalescence

Volume is conserved when two bubbles of radius \( r_1 \) and \( r_2 \) collide such that the new bubble size is given by:

\[
 r_3^3 = r_1^3 + r_2^3 \quad \ldots \ldots (3.22)
\]

The resultant bubble contains a pressure \( P_3 \) given by:

\[
 \frac{4}{3} \bar{n} r_3^3 P_3 = \frac{4}{3} \bar{n} \left[ r_2^3 P_2 + r_1^3 P_1 \right] \quad \ldots \ldots (3.23)
\]

However, the true equilibrium pressure within a bubble radius \( r_3 \) is given by \( 2Y/r_3 \), and so an excess pressure \( P_{\text{ex}} \) exists such that:

\[
P_{\text{ex}} = P_3 - \frac{2Y}{r_3}
\]

The parameters \( r_3 \) and \( P_3 \) can be expressed in terms of \( r_1 \), \( r_2 \), and \( Y \) from equations (3.22) and (3.23). The surface energy decrease when two bubbles collide at constant volume is given by (86):

\[
\Delta G_s = 4 \bar{n} Y r_2^2 \left[ \left( 1 + \left( \frac{r_1}{r_2} \right) ^3 \right) ^{\frac{3}{2}} - \left( 1 + \left( \frac{r_1}{r_2} \right) ^2 \right) \right]
\]
and the strain energy in the matrix due to $P_{\text{ex}}$ is:

$$\Delta G_{\text{st}} = \frac{P_{\text{ex}}^2 V_2}{K}$$

If the gas behaves ideally the change in gas free energy is zero, and the free energy change for the coalescence stage is simply:

$$\Delta G_c = \Delta G_s + \Delta G_{\text{st}}$$

$\Delta G_{\text{st}}$ is small compared to $\Delta G_s$ so $\Delta G_c$ is negative for all values of $r_2$ greater than 0.1 nm. Thus thermodynamically coalescence should always occur.

2) Volume adjustment

Volume adjustment requires vacancy diffusion to remove the matrix strain energy in order to re-establish equilibrium. The bubble expands from $r_3$ to its final size $r_4$ such that the surface area decrease of stage 1) is erased. Hence during volume adjustment the strain and surface energy changes are equal and opposite to those given in stage 1) i.e. $-\Delta G_{\text{st}}$ and $-\Delta G_s$, respectively. The free energy change $\Delta G_{\text{vol}}$ on adjustment is:

$$\Delta G_{\text{vol}} = -\Delta G_s - \Delta G_{\text{st}} + \Delta G_g$$

Here $\Delta G_g$ is the gas free energy change which is given by:

$$\Delta G_g = -(n_1 + n_2) kT \ln \left[\frac{V_4}{V_3}\right]$$

The total free energy change for stages 1) and 2) is simply:

$$\Delta G_{\text{tot}} = \Delta G_c + \Delta G_{\text{vol}}$$

which reduces to

$$\Delta G_{\text{tot}} = \Delta G_g$$

$\Delta G_{\text{tot}}$ is always negative so bubbles should always coalesce and adjust their volume after collision. However,
volume adjustment requires a plentiful vacancy supply and is the slowest process at all temperatures. In view of this bubbles could be expected to contain significant excess pressures after prolonged post-irradiation annealing.

The relaxation time of two coalescing bubbles is dependent on the mechanism by which shape changes occur. If the neck between bubbles is eliminated by volume diffusion, the relaxation time \( t_v \) is (125):

\[
t_v = \frac{r_o^3 f k T}{12 D_v \gamma}
\]

where \( f \) is the correlation coefficient and \( r_o \) the final size. Alternatively, for a surface diffusion mechanism (126):

\[
t_s = \frac{4 r_o k T}{24 D_s \gamma \eta^2}
\]

where \( \eta \) is the number of diffusing atoms per unit area. Nichols (126) has shown that for \( r_o \ll 20 \) \( \mu \), \( t_s \ll t_v \) so that relaxation should usually occur via a surface diffusion mechanism. This analysis has been proposed as a method for experimentally measuring \( D_s \) in solids (127).

3.4 SUMMARY OF MECHANISMS

The two possible inert-gas bubble growth mechanisms in solids are a) re-solution of small bubbles in preference to larger ones i.e. analogous to Ostwald ripening, and b) bubble migration and subsequent coalescence. The factors limiting mobility in the latter mechanism - namely, surface diffusion, volume diffusion, vapour transport, or step nucleation - effectively control the bubble growth rate. The actual growth mechanism of a bubble population during post-irradiation annealing, and the controlling kinetics, can be deduced from a logarithmic plot of the characteristic bubble size and the annealing time. The slope of the graph...
indicates the particular operating mechanisms. The theoretical $r \text{ vs } t$ relationships have been outlined in this chapter, and are summarized by the schematic $\log r/\log t$ plots shown in Fig. 3. The theoretical slopes are given in brackets in this figure.
CHAPTER 4  THE INFLUENCE OF MICROSTRUCTURE AND EXTERNAL CONSTRAINTS ON BUBBLE BEHAVIOUR

4.1 INTRODUCTION

Random migration and coalescence of bubbles occurs in a manner analogous to Brownian motion. However, a directional drift velocity can be imposed on Brownian motion by the temperature and stress gradients produced during reactor operation. Similarly, microstructural features such as dislocations, grain boundaries, and precipitates, can significantly influence bubble behaviour. This chapter briefly reviews the effects of the above features on bubble mobility.

4.2 TEMPERATURE GRADIENTS

Barnes and Nelson (73) proposed that if a thermal gradient exerts a force greater than $10^{-12}$N on a bubble, then a directional drift is imposed on its Brownian motion so that it moves up the gradient. Experimental observation of this phenomenon is reported for He bubbles in Cu (83), gas-filled pores in Tungsten (128), and fission gas bubbles in nuclear fuels (104, 105). The force $F_a$ acting on an atom, due to a linear temperature gradient $dT/dx$, tending to move that atom down the gradient is given by (85):

$$F_a = -Q_i \frac{dT}{T} \frac{d}{dx}$$

Here $Q_i$ denotes the heat of transport for a surface or volume diffusion mechanism, and the heat of evaporation for vapour transport. The resultant force on a spherical bubble tending to move it up the gradient is then given by Nichols (86) and Shewmon (85) in the form:

$$F_b = -K r^3 F_a \quad \ldots \ldots \ldots \ldots \ldots (4.1)$$
where \( K \) is a constant. The radius dependence of the velocity can be derived by substituting equation (4.1) and the relevant \( D_b \) into the Nernst - Einstein relationship (equation (3.4)). For surface diffusion controlled bubble migration, Shewmon (85) gives the velocity in a thermal gradient as:

\[
v = \frac{2 D_s \delta Q^*_s}{r kT^2} \frac{dT}{dx} \quad \cdots \cdots (4.2)
\]

This \( r^{-1} \) dependence is also given by numerous other researchers (73, 83, 86). Similar analyses for the other diffusion control mechanisms also give \( v \propto r^n \) where \( n \) can be quite different from that predicted for random migration. A summary of the \( r^n \) dependence of velocity - with, and without, a thermal gradient - is given for diffusion controlled migration in Table 6 (73).

<table>
<thead>
<tr>
<th>MECHANISM</th>
<th>Variation of bubble velocity at constant temperature with ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Const. ( F )</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td>( r^{-4} )</td>
</tr>
<tr>
<td>Volume diffusion</td>
<td>( r^{-3} )</td>
</tr>
<tr>
<td>Vapour transport</td>
<td></td>
</tr>
<tr>
<td>1) ( D \propto r )</td>
<td>( r^{-2} )</td>
</tr>
<tr>
<td>2) ( D = ) const.</td>
<td>( r^{-3} )</td>
</tr>
</tbody>
</table>

Table 6 : The modification of the radius dependence of bubble velocity by a thermal gradient (73).

Some interesting conclusions regarding the effect of small amounts of impurities on the drift velocity up the \( \epsilon \) gradient, can be drawn from the rigorous analysis of Krivoglaz and Osinovskiy (129). It was shown that the drift velocity could be reduced or increased by small amounts of...
impurity. The magnitude, and manner, of the effect would be
governed by the surface or lattice mobility of the impurity
introduced. Although this analysis is theoretical it would
appear that alloying could have a significant effect on
bubble behaviour in temperature gradients.

Thermal gradients are particularly important
in nuclear fuels where \( \sim 1000^\circ\text{C/cm} \) often exists. Martin (24)
however, has considered that the maximum gradient in a Niobium
first-wall would be \( \sim 250^\circ\text{C/cm} \). This will still cause
extensive biasing which will result in differential swelling
across the section, and eventually exfoliation of the
plasma-side surface.

### 4.3 STRESS GRADIENTS

All materials are subjected to stress
in their working environment. The stress gradients present in
fusion reactor first-walls from macroscopic loading, and
temperature differentials, will also impose a directional
bias on inert-gas bubble migration. Barnes and Nelson (73)
have given the magnitude of this biasing force on a spherical
bubble in a linear stress gradient \( \frac{d\sigma}{dx} \), as:

\[
F = 8\pi r^3 \frac{d\sigma}{dx} \quad \ldots \ldots \ldots (4.3)
\]

Although the derivation of this equation has not been given
it does suggest that bubbles would tend to migrate to high
stress regions. More precise analyses are presented by
Eyre and Bullough (124), and Nichols (130), who have
considered that the driving force arises from the reduction
in stain energy of the solid when the bubble moves up the
gradient. Hence, Eyre and Bullough (124) give:

\[
F = \frac{\pi r^3 \sigma}{4G} \left( \frac{-3\sigma + 8\gamma}{-3\sigma + 4\gamma} \right) \frac{d\sigma}{dx} \quad \ldots \ldots \ldots (4.4)
\]

where \( G \) is the shear modulus of the solid, \( P \) the gas pressure,
and \( \gamma \) the surface tension.
However, the equilibrium condition for a bubble subjected to a tensile hydrostatic stress $\sigma_t$ is (131):

$$ P + \sigma_t = \frac{2Y}{r} \quad \ldots \ldots (4.5) $$

Hence a bubble moving in a stress gradient is subjected to varying degrees of $\sigma_t$ which means that the bubble must constantly change its size to maintain the equilibrium condition set out in equation (4.5). The force on the bubble due to the imposed stress gradient can be calculated from the work done by the bubble in changing its volume, and surface area, to maintain equilibrium. Martin (131) has investigated this situation for both tensile and compressive applied stresses, and has given the biasing driving force due to a tensile gradient $d\sigma_t/dx$ as:

$$ F = -\frac{4\pi r^4}{(4\gamma - 3\sigma_tr + \frac{3brP^2}{kT})} \cdot \text{grad} \sigma_t \quad \ldots (4.6) $$

where $b$ is Van der Waals constant and $P$ the gas pressure given by equation (4.5). A similar relationship is obtained for compressive gradients.

Martin (131) has also shown that except for very small ($r<1 \text{ nm}$) bubbles, the reduction of strain energy contribution to the driving force is comparatively small. Furthermore, unlike the predictions of Nichols (130), Eyre and Bullough (124), or Barnes and Nelson (73), equation (4.6) and its compressive stress counter-part, predict that bubbles will migrate to low stress regions independent of the nature of the applied stress. This treatment, however, is invalid for very large $\sigma_t$ because in this situation bubbles are unlikely to attain equilibrium (see later).

More recently, Speight (132) has evaluated stress-gradient/bubble interactions in terms of thermodynamics. If a) the gas obeys the ideal gas laws, and b) the bubble is allowed to change volume in order to retain equilibrium with the local stress, then the force experienced by a bubble in a tensile stress gradient is expressed in
equation (4.7).

\[ F = \frac{2\pi (Y_s - Y)}{G} \left\{ Pr + (Y_s - Y) \right\} \frac{dr}{d\sigma} \frac{d\sigma}{dx} \quad \ldots \quad (4.7) \]

Here \( Y_s \) is the surface energy, \( Y \) the surface tension, and \( P \) the gas pressure.

The gradient exerts no force on an equilibrium bubble if \( Y_s = Y \) because the bubble presence causes no distortion of the surrounding stress field. The derivative \( dr/d\sigma \) in equation (4.7) is always positive because the equilibrium bubble size increases as the applied stress becomes more tensile. Consequently, if \( Y_s \neq Y \) a biasing driving force exists and the direction of migration is determined by the sign of \( (Y_s - Y) \). If \( Y_s > Y \) the bubble moves to regions of higher tension (lower compression), but if \( Y_s < Y \) it will migrate to areas of low tension (high compression). Bubble-stress interactions resulting in biased migration are therefore complex and dependent not only on the nature and magnitude of the applied stress, but also fundamental material properties such as surface energy. However, the magnitude of stress induced biasing is considered to be small compared to that derived from thermal gradients, and consequently is unlikely to cause any increase in gas bubble swelling (24).

Stress not only biases bubble migration, but also produces breakaway growth under certain conditions. If a tensile hydrostatic stress is applied to a bubble having a stress-free radius \( r_0 \) it will expand to fulfill the equilibrium condition given in equation (4.5) - provided plenty of vacancies are available. Since the number of gas atoms is conserved when the bubble is stressed, \( P_r r_0^3 = P_r r^3 \), a critical level exists above which equilibrium cannot be attained (134). If the stress expands the bubble to radius \( r \), the equilibrium stress is given by (133, 134):

\[ \sigma = \frac{2Y}{r} \left\{ 1 - \left( \frac{r_0}{r} \right)^2 \right\} \quad \ldots \quad (4.8) \]

This equality cannot be met for stresses greater than a critical value \( \sigma_{\text{crit}} \). Stiegler (134) has given this as
At this stress the critical bubble size is \( 1.73r_0 \). If the applied tensile stress \( \sigma \) is such that \( \sigma < \sigma_{\text{crit}} \) the bubble will expand by no more than 73%, but if \( \sigma > \sigma_{\text{crit}} \) equilibrium cannot be attained and those bubbles exceeding \( 1.73r_0 \) will breakaway and possibly lead to fracture. In general, if the applied stress has a hydrostatic tensile component greater than the pressure inside an unstressed bubble, breakaway growth should be expected (133). The embrittlement of grain boundaries by Helium bubbles is a well-known phenomenon in irradiated metals. Lewthwaite (135) has shown that \( \sigma_{\text{crit}} \) is lower for boundary bubbles and consequently fracture should be initiated at the boundary rather than in the matrix. High bubble concentrations at boundaries therefore have dramatic effects on mechanical properties.

4.4 DISLOCATIONS

Bubble - dislocation interactions arise from two sources, namely a) the dislocation stress field which produces an attractive force on a bubble in an analogous manner to that described in section 4.3, and b) an inhomogeneity interaction because the bubble is a 'soft' spot in the matrix (134). Weeks et al. (136) have derived expressions for the interaction energies of a bubble with straight screw and edge dislocations in isotropic solids, by assuming bubbles to be spherical inclusions having zero bulk and shear moduli. For a bubble radius \( r \) having position co-ordinates \((R, \theta)\) about the dislocation line:

\[
\sigma_{\text{int}}^{\text{screw}} = \frac{5 G b^2 r^3}{2 \pi R^2} \left( \frac{1 - v}{7 - 5v} \right) \quad \ldots \ldots (4.10)
\]
Here \( b \) is the Burgers vector, \( v \) Poisson's ratio, \( G \) the shear modulus of the matrix, and \( K' = \left\{ (7 - 5v)(1 - v) \right\}^{-1} \). Similar expressions to equation (4.10) for screw dislocations are given by Lin and Mura (137), and Willis et al. (138).

The above relationships are only valid for \( R > 5r \) due to stress field complexities at the dislocation core. However, the maximum short range interaction energy with a screw dislocation is estimated to be (136):

\[
E_{\text{int}}^{\text{screw}} = -\frac{Gb^2r}{2\pi R^2} \left\{ 1 - \frac{(1 + 6v - 5v^2\sin^2\theta)}{5} \right\} K' \quad \ldots (4.11)
\]

where \( R_0 \) is the core radius. The long-range attractive force experienced by a bubble can be derived by differentiating equations (4.10) and (4.11) with respect to distance \( R \) from the dislocation, ie.

\[
F = -\frac{dE_{\text{int}}}{dR}
\]

This produces \( F \propto (r/R)^3 \) for both edge and screw dislocations. Willis et al. (138) have found the same size and distance dependence for screw dislocations while Lin and Mura (137) give more complex equations which reduce to the same \( (r/R)^3 \) dependence for isotropic materials. The attractive force due to an edge dislocation is more difficult to quantify because of the complexity of its stress field. It is unlikely to be as simple as suggested above, and more likely to contain terms derived from the pressure within the bubble — for example, see Ref. 124.

Once attached to a straight dislocation the bubble is at a position of minimum energy because a length of dislocation line equivalent to a bubble diameter would have to be created if the bubble was removed. Consequently the bubble pins the dislocation and the dislocation restricts bubble migration to along its line only. When the dislocation
is stressed the bubble produces a pinning force $F_p$. The dislocation will bow out between bubbles but can only move as rapidly as the bubble migrates with it. Alternatively, if the solid is free from applied stress, and bubbles are migrating in a temperature gradient, for example, a dislocation will restrain bubble mobility - again with a pinning force $F_p$. This force $F_p$ is given by Barnes and Nelson (73) and Nichols (86) as:

$$F_p = Gb^2 \cos \varphi \quad \ldots \ldots \ldots (4.12)$$

$G$ is the shear modulus, $b$ the Burgers vector, and $\varphi$ the half-angle made between the two dislocation segments at their points of intersection with the bubble surface. The maximum pinning force results when $\cos \varphi = 1$, i.e. $F_p = Gb^2$.

To remove a bubble from the dislocation a force greater than $F_p$ is required. If such a force is supplied by a thermal gradient bubbles must be of a critical size before they will detach from the imperfection (86). The driving force due to a temperature gradient increases with increasing bubble radius, and is given by equation (4.1) as:

$$F_b = \frac{KQ^*_s r^3}{T} \frac{dT}{dx} \quad \ldots \ldots \ldots (4.13)$$

where $K$ is a constant at any temperature $T$. Equating this to $F_p$ with $\varphi = 0$ yields:

$$r_c = \left[ \frac{T Gb^2}{KQ^*_s \frac{dT}{dx}} \right]^{\frac{1}{3}} \quad \ldots \ldots \ldots (4.14)$$

All bubbles smaller than $r_c$ remain attached while those greater will break away from the dislocation.

In the situation where the driving force for dislocation motion, and bubble breakaway, are both small the bubble is confined to migration along the imperfection line only. Speight (139) has calculated the coalescence time for bubble pairs assuming a surface diffusion mechanism, and finds $\tau \propto t^{-1/7}$. Similar findings are also reported by Aitken et al. (95). Beeré (118) has interpreted bubble migration down
stationary dislocations in Cu in terms of the step-nucleation model. Bubbles moved faster along a dislocation than in the matrix because surface steps introduced by the imperfection reduce the critical ledge nucleation energy. To summarize, therefore, the interaction of bubbles with both edge and screw dislocations is determined by the magnitudes of the relevant driving forces within the material. Bubbles can migrate along the imperfection line as well as impeding dislocation motion.

4.5 GRAIN BOUNDARIES

When bubbles are present at grain boundaries the combined free-energy is lowered because a) an area $\sim \pi r^2$ is removed by a single bubble, and b) $\gamma_{gb} < \gamma$ so that a bubble locally adjusts to maintain $P = 2\gamma/r$. Three types of interaction are possible depending on the driving force for boundary motion $F_{gb}$, the bubble pinning force $F_p$, and the size and volume fraction of bubbles present (114):

1) If $F_p \gg F_{gb}$ the boundary is pinned by the intersecting bubbles.

2) If $F_{gb} \gg F_p$ the boundary easily breaks away from the bubbles, and finally

3) If $F_{gb} \sim F_p$ a moving boundary will drag bubbles with it. This phenomenon is particularly important because sweeping of bubbles leads to high boundary populations, increased coalescence, and severe localized swelling leading to embrittlement.

The conditions necessary for boundary sweeping are given by Greenwood and Speight (140) who have also shown that bubbles detach from the boundary at a critical size. If $\Delta F$ is the free energy change when an atom moves from one grain to the next across a boundary (i.e. the driving force for boundary migration), the criterion for detachment of the bubble is contained within equation (4.15).
\[ F > \frac{\pi r a^3 \gamma_{gb}}{12} + \frac{3 a^5 f \gamma_{gb}}{8 r^3} \exp \left( \frac{Q - Q_s}{kT} \right) \] ......(4.15)

Here \( a^3 \) is the volume of an atom, \( l \) the bubble spacing in the boundary, \( f \) an entropy factor, \( Q \) the activation energy for boundary movement, and \( Q_s \) the activation energy for surface diffusion. The right-hand side of equation (4.15) is a minimum if

\[ r^4 \frac{3 a^2 f l^2}{8 \pi} \exp \left( \frac{Q - Q_s}{kT} \right) \] ......(4.16)

Thus for a given driving force and bubble spacing, a critical size exists for detachment from the boundary.

The boundary, therefore, sweeps bubbles until coalescence within its plane produces bubbles of critical size. The coalescence rate of bubbles within the boundary plane is an important factor which can be estimated from the pair-wise coalescence time given by Wolfenden and Farrell (74) as:

\[ t_c = \frac{l^4}{32 r^2 D_b} \] ..........(4.17)

On the basis of Greenwood and Speight's (140) model one would expect to see boundaries decorated with small bubbles rather than large ones. Macdonald (141) has observed this in U - 4.7% C where strings of small bubbles outlined the boundaries while larger ones marked the earlier boundary positions. Shiraishi et al. (116) have also interpreted the occurrence of large bubbles in He bombarded Al using a bubble sweeping model.

An extensive experimental investigation of He bubble sweeping in Cu is reported by Pati and Maiya (114). They have measured the boundary migration distance \( x \) (i.e. the width of the bubble denuded zone adjacent to the boundary) as a function of annealing time and temperature, to study the kinetics of sweeping. The bubble restraining force \( F_p \) is given by numerous authors in terms of the boundary tension \( \gamma_{gb} \), the
bubble size $r$, and $\theta$ the half-angle of the cone defined by
the intersection of the boundary with the bubble ($73, 86$).

$$F_p = \pi r \gamma_{gb} \sin 2\theta \quad \ldots \ldots \ldots (4.18)$$

For sweeping the boundary migration driving force $F_{gb}$ must
equal $F_p$. For $\theta = 45^0$, $F_p$ is a maximum and $F_{gb}$ can be
expressed as (114):

$$F_{gb} = \frac{N_s \pi r \gamma_{gb}}{N_v} \quad \ldots \ldots \ldots (4.19)$$

where $N_s$ is number of bubbles per
unit area on the boundary, and $N_v$ is the total number of
bubbles per unit volume.

The boundary migration rate is governed by how
fast the bubbles can move with it and so the Nernst-Einstein
equation can be expressed in the form:

$$\frac{dx}{dt} = \frac{D_{gb}}{kT} F_{gb}$$

The boundary migration distance is therefore related not only
to time at temperature, but also to the kinetic mechanism
limiting bubble mobility - i.e. via $D_b$. Pati and Maiya (114)
have found that the boundary migration rate in Cu was an
order of magnitude slower than predicted by surface diffusion
kinetics, and concluded that step-nucleation probably
limited bubble migration. This conclusion is in complete
agreement with that of Willertz and Shewmon (110) for
randomly migrating He bubbles in Cu.

It should be emphasized at this point that
bubbles have little effect on boundary migration if $F_{gb} > F_p$.
For example, Beere (142) - investigating boundary/bubble
interactions in He - implanted Cu when $F_{gb} > F_p$ - has
reported that the boundary remained flat when passing through
the cavities. Bubbles, unlike precipitates, have very little
influence on boundary migration under these conditions.
Similarly, Coleman (115) also found He bubbles with \( r > 3 \) mm were ineffectual in impeding boundary motion in thin Au foils. Bubble-boundary interactions are, therefore, dependent on the metallurgical state of the metal. Sweeping is likely in recrystallized materials where \( F_{\sigma b} \) is low, but not in the cold-worked condition where a high driving force for recrystallization exists.

4.6 PRECIPITATES

It was recognized many years ago that nuclear fuels containing second-phase dispersions exhibited lower swelling than precipitate free materials. This reduction in swelling is largely due to fission-gas bubble pinning at these particles, such that bubble migration and gas release to grain boundaries is severely limited. Kramer, Johnstone, and Rhodes (143) observed bubbles attached to second-phase particles in irradiated U-4%Mo, and reported volume swellings only a tenth of those in un-adjusted fuel. Similarly, bubbles have been observed attached to small Uranium particles in Th-U (144). The best swelling characteristics occur when high numbers of very fine precipitates or particles are present (143) because potentially more bubbles can be trapped. However, to be effective, the second phase must be relatively stable during irradiation because no swelling advantage is obtained if they all dissolve (73).

A bubble changes size and shape when it encounters a precipitate, in order to create a balance between the various surface and interfacial tensions, and minimize the total free-energy of the system. The binding energy \( E_b \) of the two can be calculated from the changes in surface and interfacial tensions, and the expansion of the gas to its new equilibrium pressure. Brinkman and Johnstone (69) have estimated \( E_b \) for the case of a flat, rigid, precipitate, but a more rigorous analysis has been presented by Nelson (145) for both flat and spherical, rigid precipitates, and flat
FIG 4 : The binding of a gas bubble to a) a flat rigid precipitate, b) a spherical rigid precipitate, and c) a flat non-rigid precipitate (after Nelson (145)).

precipitates which can change shape when a bubble attaches. A simplified geometric representation for each of these situations is given in Figure 4. Here $\theta$ is the contact angle, $\gamma_s$ the surface tension of the matrix, $\gamma_p$ the surface tension of the precipitate, and $\gamma_{ps}$ the interfacial tension between the precipitate and matrix.

If the bubble has a radius $r_1$ in the matrix and the gas obeys the ideal-gas laws, the binding energy $E_b$ to a flat, rigid, precipitate - Fig. (a) - is given by Nelson (145) as:

$$E_b = -8\pi r_1^2 \gamma_s \ln 2 \left\{ 4 - (1 - \cos \theta)^2 (2 + \cos \theta) \right\}^{1/2}$$
Binding is strongest for high $\Theta$. Since $\Theta$ is related to the surface and interfacial tensions by a simple tension balance (e.g., from Fig. 4 (a) $\gamma_p = \gamma_s \cos \Theta + \gamma_{ps}$), this implies that binding will be strongest for high $\gamma$. If the precipitate is not flat but spherical - see Fig. 4 (b) - Nelson (145) has shown that there is no net change in surface or interfacial energies when a bubble becomes attached. The binding energy arises only from the free-energy change of the gas which is simply:

$$E'_b = -\frac{8\pi r_1^2 \gamma_s}{3} \ln \frac{r_2}{r_1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4.20)$$

where $r_2$ is the bubble radius when attached to the precipitate.

However, Markworth and Baroody (146) have re-analysed this particular situation to show that there is a net interfacial energy change, of the same order of magnitude as the gas free-energy change, for certain values of $\alpha$. ($\alpha$ is the angle between the chord of contact and the tangential tension as shown in Fig. 4 (b)). Under certain conditions, therefore, binding is particularly strong.

Further contributions to $E_b$ will also arise from the presence of stress fields around particles - although this situation has not been sufficiently quantified as yet. The final situation Nelson (145) considered was binding to a flat, non-rigid precipitate, which altered its shape when attached to a bubble to produce the form shown in Fig. 4 (c). $E_b$ was again found to be given by equation (4.20), where $r_2$ is now the radius of curvature of the matrix-gas interface when attached to the bubble.

A precipitate exerts a restraining force $F_p$ on a bubble which is related to $E_b$ via $F_p \propto E_b/r_1$ (124). Hence $F_p \propto r_1$ regardless of precipitate morphology. Dislocation and grain boundary motion are unlikely to remove bubbles from second-phase particles, but temperature gradients in nuclear fuels may reach levels where the force exerted is sufficient.
to overcome the precipitate restraining force. Precipitate-bubble interactions are not limited to nuclear fuels but often occur in more conventional materials. Ruedl (147) has reported bubble trapping at Al$_2$O$_3$ particles in He$^+$ irradiated Al - 2.5% Al$_2$O$_3$ alloys, and Kramer et al. (148) have noted He bubbles attached to carbides - particularly at grain boundaries - in type 304 stainless-steel. Although precipitate-cavity interactions control swelling in fuels, such interactions at grain boundaries in structural materials may result in fracture initiation and embrittlement. The nature and consequences of cavity-precipitate interactions in these metals requires further quantification.
5.1 INTRODUCTION

Niobium and its dilute alloys can dissolve large quantities of interstitials even when annealed under vacuum (149). Oxygen and Nitrogen are of particular importance because they influence hardness, mechanical properties, and even magnetic susceptibility (150). Furthermore, the segregation of these elements to void and bubble surfaces during irradiation, has been proposed as an explanation for the ordered cavity arrays frequently observed in refractory metals (151). Potentially, therefore, interstitials can interfere with bubble growth. To minimize this interference all heat-treatments undertaken in this investigation were performed under ultra-high vacuum (UHV) conditions. The subsequent analysis of bubble populations in Nb and Nb-Zr alloys, using transmission electron microscopy, has enabled the He bubble growth mechanism and controlling kinetics to be deduced.

5.2 UHV HEAT-TREATMENT

5.2.1 The vacuum system

The UHV system used for all heat-treatments is shown diagrammatically in Figure 5. It was designed and supplied by Vacuum Generators LTD, and it consists of an EN 58E (AISI 304L) stainless-steel, cylindrical chamber, which is pumped at \( \sim 230 \text{ l.sec}^{-1} \) by an Edwards E04 diffusion pump containing a polyphenyl-ether, low vapour-pressure, oil. This pump has a 5 litre liquid-Nitrogen cold-trap, and is backed by a rotary pump which features the usual foreline-trap and gas ballasting facilities. The backing and roughing lines are also constructed of stainless-steel. The vacuum chamber itself has an internal diameter of 30 cm, and a height of 82 cm.
Figure 5: The UHV system
It features two diametrically opposed viewing ports, eleven 8 cm diameter accessory ports, and a 25.4 cm diameter main entry port. All port seals are of the metal knife-edge type using Cu gaskets. The two viewing ports are protected from radiant heating during furnace operation by stainless-steel heat-shields which are adjustable from outside the chamber.

A Titanium Sublimation Pump (TSP), which helps to maintain good vacuum at high temperature, has been incorporated close to the base of the chamber. The TSP assembly, and the baffle valve to the diffusion pump, are protected from falling objects by a stainless-steel plate which also serves as a heat-shield. An Ion Gauge is used for pressure measurement within the chamber, while Pirani gauges monitor the backing line pressure. Furthermore, a VG Micromass 2 mass-spectrometer has been used to provide qualitative information about vacuum constituents before, during, and after heat-treatment.

When sample changing is necessary the main entry port must be detached to provide access to the furnace. To facilitate this the chamber must be returned to atmospheric pressure. Air may be bled into the chamber for this purpose, but it has the disadvantage of introducing a) all the elements that could contaminate the sample at high temperature, and b) large quantities of water vapour which adsorbs on internal surfaces increasing pump-down times and causing vacuum degradation by outgassing during furnace operation. In this investigation high-purity (99.999%) Argon was used rather than air, and the approach of the chamber to atmospheric pressure was monitored using a simple device incorporated into the gas flow line. This device - which is illustrated in Figure 6 - consists of a straight glass tube through which Ar flows, with a ball-bearing 'pressure release valve' (marked A in Figure 6) operating in one direction perpendicular to the gas flow. This valve is kept vertical so that the ball-bearing seats in the position shown in Figure 6 under normal conditions. Attached to the valve is a reservoir - marked B - containing diffusion pump oil.
Initially the Ar flow-rate into the UHV chamber is adjusted to produce a low bubbling rate through the diffusion pump oil in the reservoir. If the flow-rate remains constant reservoir bubbling becomes more violent as the chamber pressure increases, because more gas is diverted past the valve. When the bubbling becomes particularly violent the flow-rate is reduced and the whole process repeated. Eventually the gas flow-rate is minimal and the chamber pressure is close to 760 Torr Ar. At this point the flow-rate was significantly increased to ensure that a constant stream of Argon flowed through the open access port during specimen changing. The use of Ar has much improved subsequent pump-down times, as well as outgassing characteristics on heating.

5.2.2 The Furnace

The furnace is cylindrical and supported on a stainless-steel bracket (but isolated from direct contact by ceramic insulators) in the position shown in Fig. 5. The furnace casing has a length of 18 cm, an external diameter
of 10 cm, and the casing thickness is such that the internal diameter is \( \approx 7 \) cm. The furnace is constructed entirely of Molybdenum sheet and its main features are illustrated in figure 7.

The heating elements are composed of 1 mm diameter Mo wire, and their total resistance is \( \approx 3.5 \) ohms. Electrical connection to these elements is made through a fixed Mo end-cap - see Figure 7. The other end-cap is removable to allow specimen positioning from the open UHV entry-port. The power-
supply can continuously deliver a maximum of 40 amps a/c and so the furnace power rating is theoretically ~ 5.6 kW. In practice, however, currents of up to 25 A are sufficient to maintain 1350°C which represents the highest prolonged annealing temperature used in this work.

Samples for heat-treatment were positioned at the centre of the furnace on a Mo tray. Direct contact with the tray was avoided by seating the sample on a Tungsten wire mat - this eliminated 'diffusion welding' of the sample to the tray during prolonged high temperature anneals. The sample temperature was monitored by a closely-positioned Pt/Pt-13%Rh thermocouple which was also used, in conjunction with an automatic Eurotherm Temperature Controller, to control the current supplied to the furnace. The furnace casing has a 0.5 cm diameter hole drilled in its side so that the sample can be seen (when hot) from one UHV viewing port. Optical pyrometry was therefore used to check thermocouple readings, and generally discrepancies of ±10°C were observed.

The furnace heating rate and the systematic vacuum deterioration are given in Figure 8 a) and b) respectively, for typical final temperatures of 950°C and 1350°C. The most notable feature is that the vacuum rarely deteriorates beyond ~ 2 x 10^-6 Torr even though the heating rate is ~ 100°C/min. The major vacuum constituents were found to be N₂, H₂O, and CO, with much smaller amounts of O, Ar, and H₂ also in evidence. Generally, with prudent use of the TSP, the vacuum at temperature was improved to ~ 10^-7 Torr or better within 1 to 2 hours. During heating the time spent at temperatures below the final one, where bubbles are mobile, is small and insignificant except for short (up to 1 hour) anneals. However, the cooling rate is equally important but more dependent on the annealing time and temperature. Generally the furnace took about half an hour to cool down to 650°C after 100 hour anneals at 1050°C. Bubble growth during heating and cooling periods is therefore unlikely to introduce serious errors to the overall growth mode operating at the final annealing temperature.
FIGURE 8a: The rate of approach to heat-treatment temperature.

FIGURE 8b: Vacuum variation during the temperature rise of Fig. 8a.
The ability of Nb to retain large quantities of O, N, and C in solid-solution at high temperatures is well-known. Seybolt (152) investigated O solubility using X-ray and metallographic methods, and found the solubility limit at 1100°C to be \( \approx 5.5 \text{ at.\%} \) (1.0 wt.%). Elliot (153) however, obtained a slightly lower value of 2.9 at.% at 1000°C. Nitrogen solubility in Nb has been investigated by numerous researchers, but Cost and Wert (154) have produced an empirical equation describing the terminal solubility above 1150°C, ie:

\[
x = 720 \exp \left( -\frac{20,000}{RT} \right)
\]

Here \( x \) is the atomic percentage of N, \( R \) the Universal gas constant (in cal/mol K), and \( T \) the absolute temperature. Equation (5.1) predicts the Nitrogen solubility limits at 1150°C and 1600°C to be \( \approx 0.5 \text{ at.\%} \) and \( \approx 3.1\text{at.\%} \), respectively. The solubility of Carbon is less easily characterized but is in the order of 2.0 at.% between 1600°C and 1700°C (155).

For Nb containing up to 10 at.% Zr the Oxygen solubility limit is reduced to below 0.5 at.% at 1050°C because of a strong tendency to form \( \text{ZrO}_2 \) (156). This reduction in solubility is also reported by Inouye (157) who has also quoted work which shows that Zr increases the Nitrogen solubility limit from \( \approx 2.2 \text{ at.\%} \) at 1400°C, to \( \approx 4.1 \text{ at.\%} \). These high solubilities make Nb and Nb-Zr alloys susceptible to interstitial pick-up from residual vacuum gases during annealing. This contamination results in a variable sample composition as a function of annealing time, which potentially complicates the interpretation of bubble behaviour. Clearly these effects must be minimized. Inouye (149) has conducted a detailed investigation of refractory metal contamination during 1000 hour anneals at temperatures between 600°C and 1200°C and under vacuums between 10^{-6} and 10^{-7} Torr. He found that a) contamination increased with increasing temperature, and b)
Figure 9: Comparative interstitial pick-up in refractory metals during 1000 hr anneals at 2.7 x 10^{-7} Torr.

Nb-1% Zr suffered more interstitial pick-up than pure Nb, Ta, or Mo - as shown in Figure 9. (The contamination of 0.62% and 2.63% Zr alloys was not significantly different from that of the 1% alloy). Over 80% of the pick-up in Nb-1%Zr was due to Oxygen, as figure 10 clearly shows, while the Nitrogen content remained constant and Carbon increased only slightly.

The wrapping of samples with other refractory metal foils was found to be particularly effective in reducing contamination. Figure 11 shows that the extent of protection is independent of the actual wrapping material which implies that the wrapper acts as a physical barrier to impinging gas molecules, rather than a chemical getter (149).

In view of these results, samples in this work were initially enclosed in a Zr box during annealing. However, some problems were experienced due to Zr evaporation from the box and condensation on the sample surface. This was eliminated by using a Nb foil liner inside the box, and the sample was isolated from direct contact by Tungsten wire supports.

Hardness is a sensitive test for interstitial pick-up in Nb (152), so that the benefits of employing a box during annealing are clearly shown by the experimental micro-hardness given
Figure 10: The contamination of Nb-1\%Zr by residual gases in high vacua (149).

Figure 11: The effect of foil wraps on the contamination of Nb-1\%Zr (149).
in Table 7. This dual Nb/Zr box arrangement was used in all stages of UHV annealing.

<table>
<thead>
<tr>
<th>Nb - AS RECEIVED</th>
<th>Nb - ANNEALED AT 1350°C / 1 HOUR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BOXED</td>
</tr>
<tr>
<td>153</td>
<td>126</td>
</tr>
</tbody>
</table>

Table 7: Vickers micro-hardness of boxed and un-boxed Nb (given as the average of fifteen readings using a 50g load).

5.3 ION IMPLANTATION

5.3.1 Materials

The metals used in the course of this work were Nb and binary Nb-Zr alloys containing 0.3 at.%, 1 wt.%, and 2.07 at.% Zr. (It should be noted that for Zr in Nb at.% and wt.% can be regarded as equivalent). The Nb and Nb-1%Zr were received as 75 μm thick sheet, while the other alloys were produced as 100 μm thick sheet from 1.5 mm diameter wire, using lateral rolling (153). The interstitial content, where known, of these materials are given in Table 8.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>WT. PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Nb</td>
<td>400</td>
</tr>
<tr>
<td>Nb-0.3%Zr</td>
<td></td>
</tr>
<tr>
<td>Nb-1%Zr</td>
<td>615</td>
</tr>
</tbody>
</table>

Table 8: The interstitial contents of the metals investigated.

In addition, one sample each of Nb containing 4, 68, 640, and 1584 wt.ppm of Oxygen was supplied by Argonne National...
Laboratory, USA. These samples were very small - the largest having dimensions 1 cm x 0.5 cm x 100 μm - but successfully provided information on the effect of Oxygen on bubble behaviour.

### 5.3.2 Specimen preparation for ion-implantation

Foil samples measuring 1.5 x 2.0 cm were degreased in Acetone, and chemically polished for 10 seconds in a mixture of 28% H_2SO_4, 11% HF, 11% HNO_3, and 50% H_2O, cooled by iced-water. Individual samples were then boxed, for the reasons given in section 5.2.3, and vacuum annealed at 1350°C for 1 hour to ensure a completely stabilized microstructure. The subsequent grain size was determined from scanning electron micrographs taken on a Stereoscan IIA operating in the specimen current mode. For Nb grains were ~ 80 μm, whereas those in Nb-1%Zr were in the range 20 - 35 μm.

To minimize ion reflection and channelling during implantation the annealed foil surface must be relatively flat. Each sample was therefore electropolished for 5 minutes in 80% H_2SO_4, 20% HF, using a Pt cathode and a constant applied voltage of 10 volts. Other H_2SO_4 - HF, or H_2SO_4 - HF - HNO_3 electrolytes were successfully used provided the HF content was not less than 12 - 15% by volume. Below this severe surface roughening was experienced due to the formation of an amorphous oxide film. Finally the foils were mounted on Aluminium plates using a high conductivity, Silver-based paint, to await implantation.

### 5.3.3 Helium implantation

Each sample had an area of 1 cm² implanted with \(^{4}\)He\(^+\) at sequential energies of 220, 140, 100, and 50 keV, using the Department of Electronic and Electrical Engineering 500 keV linear accelerator. A uniform concentration of 1 at.% He (5 x 10\(^{20}\) He/cm\(^3\)), between the range profile peaks at 50 and 220 keV, was introduced using the conditions set out in Table 9.
<table>
<thead>
<tr>
<th>Concentration $^4$He/cm$^3$</th>
<th>Energy (keV)</th>
<th>Dose for 1 cm$^2$ * (µC)</th>
<th>Max. displacement damage (dpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{20}$</td>
<td>50</td>
<td>1535.7</td>
<td>0.365</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1680.7</td>
<td>0.224</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>997.9</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>3153.3</td>
<td>0.215</td>
</tr>
</tbody>
</table>

*1 µC/cm$^2$ = 6.2418 x 10$^{12}$ He/cm$^2$

**Table 9**: The Implantation schedule for 1 at.% He

Engin et al. (159) have considered the depths of the He range profile peaks in Nb to be 210, 412, 555, and 808 nm for the energies 50, 100, 140, and 220 keV respectively. This implies that the width of the implanted band containing ~1 at.% He is ~600 nm. However, recent theoretical data published by Ziegler (160) gives the range peaks as 190, 320, 420, and 600 nm at these energies. Furthermore, Biersack et al. (63) have used a nuclear activation technique to measure $^3$He range profiles in both single crystal, and polycrystalline, Nb targets, for energies up to 350 keV. Their results agree well with Ziegler's computations so that 400 nm is probably a more realistic estimate of the thickness of material containing 1 at.% He after sequential energy implantation. The presence of small quantities of Zr will not significantly alter these range characteristics (159).

An important phenomenon regarding microstructural development during irradiation, and subsequent annealing, is displacement damage in the target. The extent of this damage can be estimated for incident light-ions of energy $E_1$, from an approximate equation given by Thompson (161) as:

$$C_d = \frac{\Phi t}{2\pi \sigma_0} \frac{Z_1^2 Z_2^2 E_1^2 E_R^2}{E_{d} E_1^E d} \ln \frac{A}{E_1}$$

...(5.2)

$C_d$ is the atomic concentration of displaced atoms (expressed as displacements per atom - dpa), $\Phi$ the ion flux, and $t$ the irradiation time - the quantity $\Phi t$ is equivalent to the dose
given in table 9. $M_1$ and $Z_1$ are the ion mass and atomic number, respectively, while $M_2$ and $Z_2$ refer to the target material. $E_R$ is the Rydberg energy (13.6 eV), $a_0$ the Bohr radius ($5.3 \times 10^{-2}$ nm), and $\Lambda$ a constant equal to $\frac{4M_1M_2}{(M_1 + M_2)^2}$. Finally, $E_d$ is the energy required to permanently displace a lattice atom.

If we assume a minimum value for $E_d$ a maximum damage level can be estimated from equation (5.2), for the dose and energy conditions given in Table 9. Jung and Lucki (162) found experimentally a minimum $E_d$ of 28 eV for Nb containing 300 ppm Zr, and so using this value with $M_1 = 4$, $M_2 = 93$, $Z_1 = 2$, and $Z_2 = 41$ equation (5.2) yields damage values which are also summarized in Table 9. It is immediately apparent from the results that He ion implantation does not introduce large damage levels in Nb. Sample temperature throughout implantation was nominally that of room temperature, however, beam heating was expected to produce a temperature rise of the order 30 - 50°C. Furthermore, the target chamber vacuum was maintained at ~5x10^-7 Torr throughout implantation.

5.4 SPECIMEN PREPARATION FOR TRANSMISSION ELECTRON MICROSCOPY (TEM).

The procedure employed to produce TEM samples from implanted and annealed foils was originally developed by Aitken (96). General improvements have been made, particularly to electropolishing conditions, so that good samples were produced from the Nb-Zr alloys as well as pure Nb. These samples must be prepared from the bubble zone which extends only ~400 nm starting ~200 nm from the surface. The technique used was to remove ~250 nm from the implanted surface using anodic oxidation and stripping, followed by electropolishing 3 mm discs from the un-implanted side until perforation. The specific conditions required to successfully perform these operations are given in the following sections.
Each implanted and UHV annealed sample was soaked in acetone, dried in warm air, and accurately weighed (to $\pm 10^{-3}$ mg) on an Oertling microbalance. A pair of fine-pointed tweezers was then clipped to one edge of each sample. This edge, and the base of the tweezers, was subsequently coated with Lacomit in a manner which left a 1.5 x 1.5 cm area on each side of the sample exposed for anodizing. Anodizing took place in 45 ml of 0.35 M/litre Na$_2$SO$_4$ solution which was cooled in an iced-water bath, and magnetically stirred. A stainless-steel cathode was employed and electrical connection to the sample was via the attached tweezers. A constant current of 22.5 mA was used and the voltage was allowed to rise to 120 V to produce a uniform emerald-green film. Arora and Kelly (163) have investigated the structure and stoichiometry of anodic films formed on Nb and conclude that generally such films are amorphous Nb$_2$O$_5$. However, for long anodizing times, large film thicknesses, or high anodizing temperatures, crystalline films tend to form which are difficult to remove. This problem was not encountered in the present work.

Anodized samples were washed in methanol rather than acetone which removes the protective Lacomit, and the oxide film was subsequently removed. Pawel and Lundy (164) added a few drops of HF to their anodizing solution to aid mechanical film removal using plastic tape. This was unnecessary in this work because the oxide was electrolytically removed (within 15 seconds) in 80% H$_2$SO$_4$, 20% HF at 30°C, with a Pt anode, the sample as cathode, and an applied potential of 1.5V. Lower electrolyte temperatures could be used with voltages up to 4 V, but much longer immersion times were required to entirely remove the film. When the film had been totally stripped the Lacomit was dissolved in acetone and dried samples were reweighed.

The weight loss $m$ from the 1.5 x 1.5 cm area exposed on each side of the sample, is related to the depth $x_A$
removed from the implanted surface, and the material density, by:

\[ x_A = \frac{m}{2 \times (1.5)^2 \times \rho} \] ...........(5.3)

The above conditions were used for Nb and the Zr-containing alloys, but usually anodizing/stripping was repeated three times to remove 250 nm from the implanted surface. Recently Diepers (165) has extended the use of the anodizing/stripping phenomenon to provide an 'in-situ' technique for electropolishing Nb intermetallics like Nb-25\%Ti, Nb-25\%Zr, and Nb\_3Sn - all of which are useful superconductors.

5.4.2 Electropolishing

To produce electron-transparent areas from the implanted zone which now occupies one surface, samples must be electropolished from the unimplanted surface. Aitken (96) has devised an apparatus - illustrated schematically in Figure 12 - which does this for 3mm discs punched from suitably prepared sheet samples. The disc is mounted, with its unimplanted surface facing the electrolyte, in the base of a PTFE container which is itself set in a Cu block surrounded by a 50 mm diameter diffusion-pump heater. It is supported in position by a spring-loaded stainless-steel tube that is connected via plastic tubing to a small funnel. Both the funnel and the tubes are filled with 1,2 Dibromo -ethane, or 1,1,2,2 Tetrabromoethane. Electrical contact to the disc (the anode) is made via the steel tube, while a Pt wire coil around the inside of the PTFE container serves as a cathode. The level of organic liquid in the funnel is arranged to be 1 cm higher than that of the stirred electrolyte during polishing. Thus, when the disc perforates this 'head' causes liquid to flow through the hole to electrically and chemically isolate the specimen, and prevent further attack. The size of perforation is also controlled by the extent of the

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Figure 12: The apparatus used for back-thinning 3 mm Nb and Nb - Zr discs (96).
To electropolish Nb, Aitken (96) used 90% H₂SO₄/10% HF at 60°C with an applied potential of 14-16 V. These conditions are similar to those used by Taylor and Christian (166) for Nb single crystals, but they invariably produced severely pitted foils - especially for the Nb - Zr alloys. Alternative conditions and electrolytes have been developed, and used routinely, to provide suitable foils from both Nb and its Zr containing alloys. A mixture containing 13% HF, 10% HNO₃, 77% H₂SO₄ at 65°C, with an applied potential of 12 V, successfully electropolished the dilute Zr containing materials. However, the most consistent results for all the materials investigated were obtained with 80% H₂SO₄, 20% HF, at 65°C and 10 V. All electrolytes were freshly prepared before use. The perforation time was dependent on the condition of the electrical contacts, and any leakage of organic liquid past the disc. Generally, however, discs perforated within 1 to 2 hours if they were ~75 μm thick. Once the disc was perforated it was removed, thoroughly washed with distilled-water followed by methanol, and allowed to dry.

Regardless of the electrolyte composition, and the operating conditions, some of the thinned-areas on each disc were obscured by a thin amorphous film. This was subsequently eliminated by dissolving the film in 20% HF, 80% H₂SO₄, at 30°C with a Pt anode and the disc as the cathode - ie. the same conditions used to remove anodic films. Dissolution only took 10 seconds, but although underlying thin areas were preserved, microscopically clean surfaces were not produced if the electrolyte temperature dropped significantly below 30°C. Throughout this operation the disc was lightly held by a pair of fine tweezers and great care was taken not to introduce extraneous dislocation structure. These electropolishing conditions, and the stain removal process when performed, produced large electron-transparent areas which were free of pits, from pure Nb and all of the Nb - Zr alloys used in this work.

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5.5 BUBBLE SIZE MEASUREMENT

5.5.1 TEM visibility conditions.

For any quantitative evaluation of bubble growth during post-implantation annealing it is essential that cavity sizes are accurately measured from TEM micrographs. A 15\% over-estimate of bubble size causes a 52\% over-estimate of the volume, which is particularly serious if the cavity volume-fraction is of interest. A detailed examination of contrast from cavities is not presented here, but the main features affecting bubble visibility are qualitatively described. The conditions used to image bubbles for measurement purposes in this study are also specified.

Contrast from small ($r < 5$ nm) cavities has many similarities to that from similar-sized inclusions. Theoretical descriptions of this contrast have been developed using the two-beam, column approximation, by Ashby and Brown (167), and particularly Van Landuyt et al. (168) for strain-free cavities. These calculations compute the intensity distribution at the bottom of the foil - i.e. the 'focus' position. Under these conditions the normal phase factors are irrelevant because they disappear in the intensity calculation (168). They cannot be ignored, however, when imaging out-of-focus (169, 170).

Three effects contribute to Bright Field contrast in two-beam, 'focus', conditions (168), namely:

1) Normal absorption - which decreases with increasing cavity size, would provide a brighter image than the background if it were the only factor controlling contrast.

2) Foil thickness: - A cavity will exhibit dark or bright contrast dependent on its position in the foil. This is due to the fluctuating nature of intensity through the foil thickness, and this contribution is independent of whether the crystal is at the exact Bragg condition or not.

3) The phase shift: - For $s \neq 0$ (where $s$ is the
deviation parameter) the presence of a cavity produces a phase shift (not to be confused with the normal phase factors) in the electron wave passing through the crystal. This shift makes the contrast strongly dependent on the magnitude of $s$, the bubble size, and its vertical position in the foil.

Cavity contrast is, therefore, very complex with, for example, two bubbles having their centres at the same positions in the foil exhibiting opposite contrast purely because of their size difference if the diffraction conditions are constant. Many of the above features have been demonstrated experimentally for cavities in TiO$_2$ (168) and Al (171). The major problem, however, is that some cavities are inevitably invisible, especially the smaller ones. Visibility is greatly enhanced by imaging 'out-of-focus'. Rühle (169), and Rühle and Wilkens (170), have published two-beam (and N-beam systematic row) calculations on the contrast expected from 'out-of-focus' imaging. Cavities imaged 'under-focus' show a bright centre surrounded by alternate dark and bright Fresnel fringes - the fringe intensity being rapidly damped after the first - while the contrast is reversed in 'over-focus' images (170). This is clearly shown for He bubbles in Nb-1%Zr by the through-focus series in figure 13. Small bubbles are clearly visible when imaged out of focus, but are effectively invisible at focus - eg. compare A in figures 13b), c), and d). Kinematical many-beam diffraction conditions, close to a $\langle111\rangle$, were used to produce figure 13. This eliminates many of the contrast variabilities obtained from dynamical two-beam images, and were the conditions used to image bubbles, with 0.75 $\mu$m 'underfocus' for measurement purposes in this work.

5.5.2 Bubble size measurement

Rühle and Wilkens (170) have analysed the correlation between image size and the true cavity size for out-of-focus imaging. For the 'under-focus' conditions used here the inside diameter of the first dark Fresnel fringe
FIGURE 13: A through focal series of small bubbles in Nb-1%Zr ([111] beam direction).

a) 1.5 μ underfocus.
b) 0.5 μ underfocus.
c) approximately focus.
d) 0.5 μ overfocus.
e) 1.5 μ overfocus.
represents the true cavity size, provided the bubble diameter is greater than 2 nm. The measurement of this dimension from TEM micrographs meaningfully describes the true size of spherical bubbles, but this is not the case for faceted cavities which project non-circular shapes. The He bubbles observed in Nb and its Zr containing alloys were clearly faceted - even for very small sizes. Their shape was either that of a \{100}/\{110\} tetrakaidodecahedron, or that of a \{100\} cube (see Chapter 6), dependent on the annealing time and temperature. Helium bubbles having \{100\} cubic morphologies have previously been reported in Vanadium (100, 101).

Smidt and Pieper (100) have measured the cube edge lengths of \{100\} bubbles in V but have not specified the exact conditions used for measurement. An unusual feature of bubbles in Nb containing 1 or 2\%Zr was the truncation along any of the \{100\} within the same grain, to produce \{100\} 'brick-shapes'. This did not affect the actual measurement of bubbles because the standardized measurement procedure developed for \{100\} cavities is not influenced by slight shape variations (provided the bubbles remain bounded by \{100\}). True bubble sizes were therefore ascertained by the following procedure:

1) TEM micrographs were taken in \{111\} orientations with the diffraction and visibility conditions specified in section 5.5.1. In this orientation \{100\} cubes, and \{100\}/\{110\} tetrakaidodecahedra, project the shape of a regular hexagon. This is shown schematically in Figure 14. Furthermore, any truncation along \{100\} still produces a hexagonal projection in this orientation - see Figure 14(b). In Figure 14(a) and 14(b) the length of each hexagon facet ie. a'b', b'c', and c'd', is related to the corresponding actual bubble dimension - ie. ab, bc, and cd, respectively - by a simple equation of the form:

\[ a'b' = ab \sin \theta \]  \hspace{1cm} \ldots \ldots (5.14)\]

Here \(\theta\) is the angle between the \{111\} beam direction and the \{100\} describing the cube edge ab (\(\theta = 54.74''\)). Hence the
FIGURE 14: Bubble projections in the [111] orientation
a) for a {100} cube, and b) for a brick-shaped bubble bounded by {100}.
measurement of three adjacent sides of the projected hexagon is sufficient to describe the orthogonal dimensions of the cavity.

2) Images were recorded in the [111] orientation at a true magnification of 120000X using a JEOL JEM 100B transmission electron microscope operating at 100 kV.

3) Micrographs were enlarged and printed at 480,000X. Bubbles were subsequently measured to the nearest 0.1 mm using a calibrated eyepiece. For this purpose the length of the inside edge of the first dark Fresnel fringe was recorded for three adjacent hexagon facets. For short annealing times in Nb-1%Zr - i.e. up to 1 hour at 950 and 1050°C - bubbles were near the resolution limit and their shape was indistinct (see, for example, some of the bubbles in Figure 13). These bubbles were characterized by three 'diameters' which were assumed to be equivalent to the length a'd' in Figure 14a. Since a'd'=2b'c' for a regular hexagon these diameters can easily be related to a cube dimension. This undoubtedly introduces errors at small sizes, but they are unlikely to be any greater than those introduced by the Fresnel fringe overlap of the true cavity size for diameters less than 2 nm. Up to 500 bubbles were measured for each annealing time, and the resultant data was inserted into a computer program which quantified the nature of the bubble population.

5.5.3 The computer analysis of measurement data

The measurement data was analysed by an Algol 60 computer program which quantified the bubble population in the following manner:

a) Each measurement was initially corrected using equation (5.4). The true volume was then computed for each bubble, summed over all bubbles, and finally averaged to provide a mean bubble volume \( V' \). The cube-root of \( V' \) gave \( M_v \) - a singular cube dimension which could be used to characterize the bubble population.

b) The volume of each bubble was calculated as
in a), but was immediately cube-rooted to assign an 'equivalent cube dimension' to each bubble. Thus any asymmetric bubbles were converted to cube dimensions, defined by their volumes. These dimensions were summed and averaged to give the mean cube dimension $M_e$ of all the bubbles sampled. Furthermore, a histogram of bubble sizes was generated from these results.

c) Finally, the aspect ratios of each bubble were calculated by dividing each measurement by the smallest. The largest aspect ratio of each bubble was summed and averaged, as were those of the other non-unity ratio. The number of bubbles within any selected ratio interval deviating from unity was also calculated. The resultant data provided qualitative information on the number and size of asymmetric bubbles, as well as giving some idea of the shape of an 'average' bubble.

The bubble population produced by a known time at temperature could, therefore, be characterized by either $M_v$ or $M_e$. Alternatively, the modal bubble size of the size histogram can be used.
A detailed examination of He-bubble shape variations with annealing time was performed for Nb-1%Zr at 1050°C. Although other samples were not examined in as much detail, the results described here for Nb-1%Zr are also representative of the features observed in alloy samples containing 2.06% Zr. Bubbles were clearly faceted at 950°C but their small size did not allow their morphology to be unambiguously determined. The bubbles produced by short anneals (ie. up to 8 hours) at 1050°C appeared as hexagons when viewed in \(\langle 111 \rangle\), and 8-sided polygons in \(\langle 100 \rangle\) and \(\langle 110 \rangle\). The three-dimensional shape consistent with these observations is that of an 18-sided tetrakaidodecahedron comprised of 6 large \{100\} facets, and 12 smaller \{110\}. Bubbles in pure Nb after 2 hours at 1050°C were also found to have this morphology, and examples of the shapes observed in \(\langle 100 \rangle\) and \(\langle 111 \rangle\) orientations are given for both Nb, and Nb-1%Zr, in figure 15. Aitken (96), in his investigation of bubble growth in Nb at 950, 1050, and 1250°C, did not specifically study shape phenomena, but a re-analysis of his micrographs reveals that shapes were essentially as described above.

For intermediate annealing times at 1050°C - ie. between 8 and 25 hours - a large proportion of bubbles in Nb-1%Zr lose their \{110\} facets to develop into \{100\} cuboids, some of which are slightly truncated along \(\langle 100 \rangle\). Beyond 25 hours the majority (in excess of 85%) of all bubbles were either \{100\} cubes or rectangular parallelepipeds ('brick-shaped' with a \(\neq b \neq c\)) bounded by \{100\}. The latter is clearly illustrated by the bubble marked B in figure 16. The interesting internal focusing contrast exhibited by this bubble arises from Fresnel diffraction caused by geometric
FIGURE 15

a) Nb-1/2Zr, 8 hours 1050°C ([100] beam direction).
b) Nb-1/2Zr, 8 hours 1050°C ([111] beam direction).
c) Nb, 4 ppm O, 2 hours 1050°C ([100] orientation).
d) Nb, 4 ppm O, 2 hours 1050°C ([111] orientation).
FIGURE 16: 'Brick-shaped' bubbles in Nb-1%Zr after 25 hours at 1050°C ([111] beam direction).

FIGURE 17: Elongated bubbles in Nb-1%Zr after 70 hours at 1050°C ([100] beam direction).
effects at bubble edges (172). Some bubbles only deviate slightly from perfect cubes, but many have aspect ratios of 4 with their long axes apparently equally distributed among the \langle 100 \rangle in the same grain. These features are illustrated in figure 17.

A further feature of anneals beyond 25 hours is that some bubbles - usually amongst the largest in a field of view - exhibit shape peculiarities apart from simple truncation. Distinct surface steps were observed to run from one side of a facet to the other in \langle 100 \rangle directions. Examples of 'stepped-bubbles' are shown in figure 18. These steps are composed generally of \{100\} planes, but occasionally \{100\} / \{110\} combinations occur - for example see bubble C in figure 18. Stepped-bubbles were not only observed in Nb-1%Zr, but also in Nb-2.07%Zr annealed at 1050°C, while this feature was not observed in pure Nb. Surface steps provide valuable information regarding the kinetics controlling bubble growth, and the nature of the pressure within the bubbles. It should be noted that bubbles shown in all the Nb-1%Zr micrographs - figures 15 to 18 - have a very uneven size distribution. However, the shape changes as a function of annealing time reported above appear equally applicable to both large and small bubbles.

Bubbles in Nb-1%Zr at 1250°C undergo accelerated growth (see section 6.4.2) but they remain a mixture of \{100\}/\{110\} tetrakaidecahedra and \{100\} cuboids. Truncation along \langle 100 \rangle was still clearly evident, but not to the extent observed at 1050°C. A few cavities, for example those shown in figure 19, have distinctly rounded \langle 100 \rangle edges which might provide a clue to the reasons for the 'breakaway' phenomenon observed at this temperature.
FIGURE 18: Stepped-bubbles in Nb-1%Zr after 25 hours at 1050°C.

a) [112] beam direction.
b) [111] beam direction.
c) and d) both [100] beam directions.
In section 6.1 it was pointed out that He bubbles in Nb-1%Zr at 1050°C have non-uniform size distributions. A similar phenomenon was also observed in Nb-2.07%Zr at this temperature. The development of very large bubbles during annealing of these two materials is clearly shown by the size histograms given in figures 30 and 34 of section 6.4. As the time at temperature increases there is a gradual extension of the histogram tails to larger dimensions. Furthermore, the development of these large bubbles in Nb-1%Zr is dramatically demonstrated by the micrographs in figure 20. No bubbles are visible in implanted but un-annealed material - e.g. figure 20 a) - whereas a fairly uniform size distribution is apparent after 2 hours at 1050°C - see figure 20 b). The populations after 8 and 70...
FIGURE 20 : The dual population at 1050°C in Nb-1/2Zr

a) Implanted but not annealed.
b) Implanted and annealed for 2 hours.
c) Implanted and annealed for 8 hours.
d) Implanted and annealed for 70 hours.
(All have a ⟨111⟩ beam direction and ~0.5μ underfocus)
The existence of irregularities in the size distributions means that great care is required when characterizing a particular distribution by a single dimension. In order to illustrate in more detail a) the features of these bubble populations, and b) the influence of large bubbles, the Nb-1%Zr size histogram after 8 hours at 1050°C is reproduced in figure 21 above. The majority of bubbles (~90%) in this figure have cube dimensions smaller than ~65 nm but the remainder have dimensions up to 5 times greater than the modal size. The histogram of sizes smaller than ~65 nm is a good fit to a theoretical 'normal' distribution curve plotted for a standard deviation of 1.35 nm. This is shown by the dotted line in figure 21 which was calculated according to standard procedures (173).

Bubbles larger than ~65 nm account for less
than 10% of the histogram population, but they contain $\sim 74\%$
of the total volume of bubbles in the sample and so greatlyinfluence the average cube dimension, $M_v$, derived from themean bubble volume. The value of $M_v$, which is clearly not thedimension that best describes the majority of bubbles, isindicated on the histogram in figure 21. The mean equivalentcube dimension, $M_e$, is also sensitive to the number and sizeof large bubbles, and so the cube dimension which bestcharacterizes the majority of bubbles is the mode of thedistribution. The modal dimension was used to describe thebubble population as a function of annealing time for all theZr-containing materials.

The deviation of $M_e$ and $M_v$ from the modalsize becomes more pronounced at long annealing times when thehistogram tail becomes more extensive and may contain $\sim 25\%$of the bubbles (after 70 hours at 1050°C in Nb-1%Zr). However,thefeatures described for the 8 hour population are equallyapplicable to other annealing times. Bubble size histograms.should always, therefore, be considered throughout anyinvestigation of bubble growth kinetics using post-implantationannealing, before characterizing the population by a singledimension.

6.3 THE EFFECT OF OXYGEN ON HELIUM BUBBLES IN Nb

Samples of Nb containing 4, 68, 640, and 1584 wt.ppm O were supplied by Argonne National Laboratory, USA. The actual amounts of each material were very small (enough for 1 or 2 TEM discs) and so a fully quantitativeinvestigation of the influence of O on He bubble nucleation andgrowth could not be undertaken. However, these samples wereimplanted using the conditions given in section 5.3.3, and thenannealed for 2 hours at 1050°C as a single batch, to precipitateand grow bubbles. The results of subsequent TEM analyses,although insufficient to deduce the specific role of O, demonstrate that this element influences a number of bubble
features. Bubble size was measured in the manner described in Chapter 5, and the density of cavities was estimated from areas of foil whose thickness had been measured (with an accuracy of $\pm 20\%$) using thickness fringes. These results are summarized in Table 10.

The bubble size histograms for each sample are shown in figure 22. The distributions for $4$, $68$, and $1584$ wt.ppm $O$—figure 22a), b) and d), respectively—have standard deviations of $\pm 1.3$ nm, whereas that for $640$ ppm is $1.8$ nm. This size distribution is therefore slightly broader than the others. There is no evidence, at this time, of any significant tail extension to larger dimensions, and consequently there is good agreement between $M_e$, $M_v$, and the modal cube size in table 10. In this situation any of these dimensions can be used with confidence to describe the population. A typical micrograph of each sample is shown in figure 23, and the faceted nature of bubbles in Nb—$4$ ppm $O$ was previously illustrated by figure 15. It was observed from these, and many other micrographs that bubbles in Nb containing $640$ and $1584$ ppm $O$ were less distinctly faceted than those produced under identical conditions in material containing Zr.

The $M_e$, $M_v$, and modal size data in table 10

<table>
<thead>
<tr>
<th>$O$ (wt.ppm)</th>
<th>No. of bubbles sampled</th>
<th>$M_e$ (nm)</th>
<th>$M_v$ (nm)</th>
<th>Histogram</th>
<th>Density No./m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Node (nm)</td>
<td>standard deviation (nm)</td>
</tr>
<tr>
<td>$4$</td>
<td>450</td>
<td>5.5</td>
<td>5.8</td>
<td>5.4</td>
<td>1.3</td>
</tr>
<tr>
<td>$68$</td>
<td>425</td>
<td>6.0</td>
<td>6.4</td>
<td>5.8</td>
<td>1.4</td>
</tr>
<tr>
<td>$640$</td>
<td>410</td>
<td>7.7</td>
<td>8.1</td>
<td>7.6</td>
<td>1.8</td>
</tr>
<tr>
<td>$1538$</td>
<td>400</td>
<td>6.4</td>
<td>6.7</td>
<td>6.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 10: Results for Nb containing $O$, after 2 hours at $1050^\circ C$. 

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FIGURE 22: Bubble size histograms for Nb containing 0 after 2 hours at 1050°C.
FIGURE 23: Bubbles in Nb containing O, after 2 hours at 1050°C.

a) 4 ppm, b) 68 ppm, c) 640 ppm, and d) 1534 ppm.
(All have a <111> beam direction).
indicates a slight increase of bubble size with increasing O content. The modal cube size data is repeated graphically in figure 2, and shows that although bubble size increases from 5.4 to 6.2 nm between 4 and 1584 ppm O, the largest bubbles are obtained at 640 ppm O. The corresponding bubble densities - also given in table 10 - show a more variable O dependence, but significantly the lowest density occurred for 640 ppm O. Thus the bubbles in Nb containing 640 ppm O exhibited a lower density, a broader size distribution, and a larger characteristic cube dimension, than those in samples with different O contents. It should be emphasised that all these results were produced from TEM specimens prepared after 240 nm had been removed by anodizing. It is unlikely, therefore, that the features reported at 640 ppm O are caused by positional variation within the implanted zone.

When the TEM samples had been produced the remaining material was subjected to 15 microhardness tests
using a 50 g load. The average Vickers microhardness number $H_v$, as a function of O content, is summarized with its corresponding standard deviation in Table 11.

<table>
<thead>
<tr>
<th>O content (wt. ppm)</th>
<th>$H_v$</th>
<th>Standard deviation</th>
<th>Seybolt Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>54</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>104</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>640</td>
<td>120</td>
<td>15</td>
<td>140</td>
</tr>
<tr>
<td>1584</td>
<td>175</td>
<td>13</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 11: The microhardness of Nb as a function of Oxygen content.

Gebhardt and Rothenbacker (174) have summarized graphically the hardness variation with O derived from the work of a number of researchers, and the results in Table 11 compare extremely well with this data. In particular, Seybolt (152) has measured $H_v$ values for O concentrations of 0.014 wt.% (140 wt.ppm) and greater, and so estimates of $H_v$ for 640 and 1584 ppm O have been made from his data. These estimates, which are also given in Table 11, are approximately 1 standard deviation higher than the experimental values reported here. Hence these hardness results not only demonstrate a sensitivity to O content, but also show that the O content of each sample hardly changed during annealing for 2 hours at 1050°C.

6.4 THE GROWTH OF He BUBBLES IN Nb CONTAINING Zr

The conventional method of analysing gas bubble growth during post-irradiation annealing is to plot the logarithm of the characteristic size against the logarithm of the annealing time. A subsequent comparison of the slope of the experimental data with those derived from theoretical equations...
for re-solution, or migration and coalescence, (these are summarized schematically in figure 3) enables the growth mode and controlling kinetics to be deduced. In this section the results for Nb-0.3%Zr, Nb-1%Zr, and Nb-2.07%Zr, are presented.

6.4.1 Nb-0.3%Zr

The cube dimensions characterizing the bubble population as a function of time at 1050°C, and the corresponding 'average' aspect ratios, are summarized in Table 12. The aspect ratio data indicates that the 'average' bubble shape, which shows little variation with annealing time, is that of a slightly truncated cube. However, this information must be regarded as only semi-quantitative because the actual ratio values are to some extent influenced by orientation, and measurement errors. The bubble size histograms—a selection of which are shown in figure 25—show some evidence of a tail extension to larger dimensions as time at temperature increases. However, very large bubbles were not apparent in micrographs to the extent illustrated previously by figure 20. Hence, although \( N_e \), \( N_v \), and the histogram modal size have slightly different values, the trend indicated by each set of data is the same. A log/log plot of the modal cube size versus the annealing time is shown in figure 26.

The data shown in figure 26 has a bubble size plateau at 3.5 nm and at ~5.8 nm. The former is present until between 8 and 15 hours when the bubble size suddenly increases until it re-saturates again at ~5.8 nm after ~30 hours. It is tempting to draw a straight line through the data and attribute these plateaux to experimental scatter. A least squares analysis reveals that the best-fit straight line through the data would have a slope of 0.13, and a correlation coefficient of 0.87. If bubbles were growing by a gas re-solution mechanism, or by migration and coalescence limited by surface diffusion, slopes of 0.5 and 0.2 (from equations 3.2 and 3.11) respectively, are to be expected. These slopes correspond to lines A and B in figure 26. It is
Table 12: Bubble size variation in Nb-0.3% Zr as a function of time at 1050°C.

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>No. of bubbles</th>
<th>$M_0$ (nm)</th>
<th>$M_v$ (nm)</th>
<th>Histogram mode (nm)</th>
<th>Aspect ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>3.5</td>
<td>4.0</td>
<td>3.5</td>
<td>1.2, 1.42</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>4.1</td>
<td>4.6</td>
<td>3.5</td>
<td>1.2, 1.50</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>4.1</td>
<td>4.6</td>
<td>3.7</td>
<td>1.16, 1.36</td>
</tr>
<tr>
<td>8</td>
<td>500</td>
<td>4.4</td>
<td>4.7</td>
<td>3.5</td>
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Figure 26: Log/log plot of modal cube size vs. time for Nb-0.3% Zr at 1050°C.
Figure 25: Bubble size histograms for Nb-0.3\%Zr at 1050°C
Figure 27: Faceted bubbles in Nb-0.3%Zr after 70 hours at 1050°C. ([100] beam direction)
immediately obvious that bubbles in Nb-0.3%Zr are not growing by a gas re-solution mechanism, while the slope of the best-fit line is also much smaller than expected for surface diffusion controlled migration and coalescence.

However, migration and coalescence limited by the nucleation of atomic ledges on a bubble facet would yield a lower slope than the 0.2 for surface diffusion control. This growth mode would explain the appearance of saturated bubble sizes and alleviate the necessity of drawing a straight line through the experimental data. Furthermore, bubbles in this material were always faceted as shown in figure 27. Qualitatively, therefore, He bubbles in Nb-0.3%Zr at 1050°C apparently grow by migration and coalescence limited by the nucleation of stable ledges on a bubble facet. This model has been developed for \{100\} cubes in Appendix II, and will be applied in a more quantitative manner in a later chapter.

6.4.2 Nb-1%Zr

Bubble size variation with annealing time in this material was evaluated for three temperatures - namely, 950, 1050, and 1250°C. The results are summarized in Table 13. The bubbles at each temperature were always faceted although those at 950°C were extremely small. Figure 28 a) and b) illustrate bubbles at 950 and 1250°C, respectively, whereas those at 1050°C were previously shown in figures 16, 17, and 20. The aspect ratios in table 13 again show little variability with time at each temperature, and suggest that on average bubbles are slightly distorted \{100\} cuboids. There are large discrepancies, particularly at 1050 and 1250°C, between the characteristic dimensions M_e, M_v, and the histogram modal size. This is explained by the development of large bubbles as described in section 6.2. The histograms at 950°C (given in figure 29) show the development of the larger dimensions with increasing time. The appearance of these larger bubbles is also visible in micrographs, as is demonstrated by some of the bubbles in figure 28a. At 1050°C - figure 30 - the tail is much more pronounced, and again develops with increasing time.
<table>
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<th>Temperature</th>
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<th>( M_V ) (nm)</th>
<th>Histogram mode (nm)</th>
<th>Aspect ratios</th>
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<td>1.5</td>
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<td>( \frac{1}{4} )</td>
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<td>7.2</td>
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Table 13: Bubble size variation in Nb-1%Zr as a function of time at 950, 1050, and 1250°C.
Figure 28:  

a) Faceted bubbles in Nb-1%Zr after 70 hours at 950°C.  
b) Faceted bubbles in Nb-1%Zr after 2 hours at 1250°C.  
(Both slightly underfocus with a [111] beam direction)
Figure 29: Bubble size histograms for Nb-1%Zr at 950°C.
Figure 30: Bubble size histograms for Nb-1%Zr at 1050 °C.
Figure 31: Bubble size histograms for Nb-1%Zr at 1250°C.
Large bubbles at this temperature were previously illustrated in figure 20. The histograms for 1250°C, which are shown in figure 31, also exhibit distinct tails - even at very short times.

The histogram modal size data for all three temperatures is plotted as a function of annealing time on the log/log plot shown in figure 32. For all anneals longer than 2 hours the 950°C data has a negligible slope which is characteristic of migration and coalescence limited by step nucleation on a bubble facet. The terminal modal size is 2.3 nm and there is no evidence of any sudden change resulting in a larger saturated bubble size. The 1050°C data in figure has a similar form to that described for Nb-0.3%Zr at the same temperature. For anneals of up to 15 hours duration the modal cube size is identical to that at 950°C - ie. 2.3 nm. This behaviour is again consistent with a 'facet-nucleation' limited, migration and coalescence growth mode. However, the bubble size dramatically increases beyond 15 hours until it re-saturates again at ~6.0 nm, after approximately 40 hours.

![Figure 32: Bubble size in Nb-1%Zr as a function of time at 950, 1050, and 1250°C.](image-url)
This second plateau is at the same bubble size to that observed in Nb-0.3\%Zr. The presence in Nb-1\%Zr of a) this upper plateau of negligible slope, and b) the crisply faceted, stepped-bubbles shown in figure 18, suggests that the growth beyond 40 hours at 1050\(^\circ\)C remains that of migration and coalescence limited by step nucleation.

The modal size results for 1250\(^\circ\)C display a very peculiar time dependence. For anneals up to 1 hour a constant size of 4.8 nm is maintained, but thereafter size dramatically rises in such a manner that there is an 8 fold increase within 25 hours. The plot in figure 32 is non-linear and so the slope, which could provide information on the reasons for this behaviour, cannot be reliably measured. There is no evidence for a re-saturated size within 40 hours. However, the large cavity sizes at this time, and the limits on available foil thickness imposed by 100 KeV microscopy, make measurements for longer times unreliable. Hence, whether or not a terminal size occurs above ~100 nm must remain unknown. Bubble growth at this temperature therefore appears complex, but it will be shown later that migration and coalescence limited by step nucleation can explain the results, provided due account is taken of the atomic processes which affect the composition of the bubble surface.

6.4.3 Nb-2\%Zr

The variation of bubble size with time at 1050\(^\circ\)C for this material is summarized in Table 14. The aspect ratios given again vary little with time, and are similar to those in Nb-0.3\% and 1\% Zr at the same temperature. The size histograms in figure 34 reveal the development of bubbles much larger than the majority, as time increases. This produces, once again, the discrepancies between \(M_e\), \(M_v\), and the modal size, which are obvious in table 14. A log/log plot of the modal size against the annealing time is shown in figure 33. The lines A and B in this figure have slopes of 0.5 and 0.2 - characteristic of a re-solution growth mode, and surface diffusion controlled migration and
<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>No. of bubbles</th>
<th>( M_c ) (nm)</th>
<th>( M_v ) (nm)</th>
<th>Histogram Mode (nm)</th>
<th>Aspect ratios</th>
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<tr>
<td>1</td>
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<td>2.0</td>
<td>2.5</td>
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<td>1.21, 1.44</td>
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<tr>
<td>2</td>
<td>500</td>
<td>2.8</td>
<td>3.6</td>
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</tr>
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<td>4</td>
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<td>6.4</td>
<td>3.1</td>
<td>1.20, 1.46</td>
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<tr>
<td>8</td>
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<td>9.6</td>
<td>6.3</td>
<td>1.25, 1.57</td>
</tr>
<tr>
<td>15</td>
<td>500</td>
<td>10.8</td>
<td>12.3</td>
<td>6.9</td>
<td>1.19, 1.54</td>
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<tr>
<td>30</td>
<td>400</td>
<td>7.5</td>
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<td>5.8</td>
<td>1.16, 1.43</td>
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<tr>
<td>70</td>
<td>480</td>
<td>7.8</td>
<td>9.3</td>
<td>6.0</td>
<td>1.17, 1.46</td>
</tr>
</tbody>
</table>

Table 14: Bubble size variation in Nb-2.07\%Zr as a function of time at 1050\°C.

Figure 33: Log/log plot of the modal cube size vs. annealing time for Nb-2.07\%Zr at 1050\°C.
Figure 34: Bubble size histograms for Nb-2.07%Zr at 1050°C.
Figure 35: Faceted bubbles in Nb-2.07%Zr after 8 hours at 1050°C.
([111] beam direction)
coalescence, respectively.

For anneals up to 8 hours the modal size progressively increases with a least-squares slope of 0.55. This is close to that expected for a re-solution growth mode, but is also near the $t^{1 \over 2}$ dependence reported for the early stages of facet, nucleation-limited, migration and coalescence in Aluminium ([113]). Anneals beyond 8 hours result in a constant modal size of $\sim 6.0$ nm. This is the same level as the upper size plateau observed in Nb-0.3%Zr, and Nb-1%Zr, at 1050°C. The presence of faceted bubbles - illustrated in figure 35 - and the negligible slope in figure 33, over this period, are pointers to a migration and coalescence growth mode, limited by step nucleation on a facet.

6.4.4 Summary

The aspect ratios summarized in sections 6.4.1 to 6.4.3 do not show any significant variation with time, Zr concentration, or temperature. Although each value represents an average which was deduced without normalizing to the particular $<100>$ directions constituting the bubble edges, they do qualitatively illustrate that some non-cubic bubbles exist in every sample. The size histograms in figures 25, 30, and 34, indicate that the development, at 1050°C, of bubbles having dimensions many times the modal size, may be related to the Zr content of the alloy. The histogram tails are much more pronounced in the 1 and 2.07%Zr materials than in Nb-0.3%Zr. Furthermore, the development of these tails is also temperature sensitive - as shown by the results in section 6.4.2 for Nb-1%Zr. At 950°C (figure 29) the tail is clearly visible for anneals in excess of 25 hours, whereas at 1050°C (figure 30) it is more pronounced and develops between 2 and 8 hours. It is present at all times at 1250°C (figure 31). The possible explanations for this feature are discussed in a later chapter.

The effect of an increasing Zr concentration
Figure 36: Modal size vs. time at 1050°C
on bubble size - and hence the growth mode and controlling kinetics - at 1050°C is summarized by the log/log plot shown in figure 36. Nb-0.3%Zr and Nb-1%Zr have constant modal dimensions of 3.5 and 2.3 nm, respectively, for anneals up to 15 hours at this temperature. Hence, the increased Zr content apparently reduces the initial saturated size whereas it increases the bubble density after 1 hour from $\sim 3 \times 10^{22}/m^3$ to $\sim 5 \times 10^{22}/m^3$, respectively. In Nb-2.07%Zr (where the bubble density after a 1 hour anneal is $\sim 7 \times 10^{22}/m^3$) the modal size progressively increases to $\sim 6.0$ nm within 8 hours and thereafter remains constant. There is no evidence of any saturation at a smaller dimension in this alloy, and the 6.0 nm level corresponds to the upper plateau observed in Nb-0.3 and 1%Zr for anneals of 25 hours and beyond. The fact that a common saturated size exists in all these materials suggests that the sudden increase in modal size to this level in Nb-0.3% and 1%Zr after prolonged annealing is related specifically to the behaviour of Zr. In the previous sections the negligible slopes of the plots in figure 36, and the presence of faceted bubbles, were concluded to provide evidence of facet, nucleation limited migration and coalescence. It will be shown in chapter 8 that the equations derived in Appendix II provide a) more quantitative evidence that this conclusion is correct, and b) information regarding the specific role of Zr, and the reasons for the two saturated sizes in materials containing up to 1%Zr.
In Chapter 6, section 6.1, numerous shape peculiarities were reported in Nb-1%Zr at 1050°C. For short anneals bubbles were composed of \{100\} and \{110\} facets, but beyond 8 hours \{100\} cubes, or rectangular parallelepipeds (brick-shaped with \(a \neq b \neq c\)) bounded by \{100\}, were developed. Some bubbles had aspect ratios of up to \(1/4\) with their long axes apparently equally distributed among the \(\langle 100 \rangle\) - see for example figure 17. Furthermore, stepped-bubbles were frequently observed for anneals in excess of 25 hours. In this chapter it will be shown that the loss of \{110\} facets, and the presence of stepped and elongated bubbles (which clearly do not represent the minimum surface energy per unit volume), can be explained by considering in detail the following items:

a) the conditions for thermodynamic equilibrium after two bubbles have coalesced,
b) the atomic processes occurring at the bubble surface (these control the rate at which the shape alters to fulfil the conditions set out in a), and finally
c) the vacancy flux available to equilibrate the pressure within the resultant bubble after coalescence.

7.1 BUBBLE EQUILIBRIUM CONDITIONS

A cavity, or a particle, at thermal equilibrium should have flat faces of low index, low energy planes, with a detailed shape governed by deep cusps in the polar surface energy \(\gamma\) plot (175). The two minimum free energy conditions for a bubble of volume \(V\), internal pressure \(P\), strain and shape parameters \(q\) and \(s\) respectively, and containing \(n\) vacancies at temperature \(T\), are summarized by
Nelson et al. (111) as:

\[ P = \left\{ \frac{\partial}{\partial V} \int \delta d\mathbf{A} \right\}_{T,s} \] \hspace{1cm} (7.1)

\[ \left\{ \frac{\delta}{\delta s} \int \delta d\mathbf{A} \right\}_{T,n,q=0} = 0 \] \hspace{1cm} (7.2)

Equation 7.1 shows that at vacancy equilibrium the gas pressure must balance the surface energy terms, while equation 7.2 is simply the condition for shape equilibrium, i.e., it defines the shape having the lowest total surface energy. In the absence of any anisotropy of surface energy the equilibrium shape will be a sphere, radius \( r \), containing a gas pressure \( P = \frac{2\delta}{r} \). If the bubble is cubic and bounded by \( \{100\} \) then \( P = 4\delta^{100}/a \) where \( \delta^{100} \) is the surface energy of a \( \{100\} \) plane, and \( a \) is the cube dimension (111).

A new bubble produced by coalescence of two smaller ones must come to equilibrium by absorbing vacancies to relieve the resultant excess gas pressure. It must also re-arrange its shape by surface diffusion. If the number of vacancies available to equilibrate the bubble is limited, and surface re-arrangement is slow, the bubble will contain an excess pressure for a significant time at a non-equilibrium shape. This will cause strain around the bubble and the free-energy conditions necessary to minimize the strain energy \( Q \), become (111):

\[ \left[ \frac{\partial Q}{\partial V} \right]_{T,s} = P - \left\{ \frac{\partial}{\partial V} \int \delta d\mathbf{A} \right\}_{T,s} \] \hspace{1cm} (7.3)

\[ \left[ \frac{\delta Q}{\delta s} \right]_{T,n,q} = - \left\{ \frac{\delta}{\delta s} \int \delta d\mathbf{A} \right\}_{T,n,q} \] \hspace{1cm} (7.4)

Equation (7.3) shows that the strain energy per
unit volume around the bubble is minimized for any excess pressure by the development of higher energy planes. Consequently if atoms diffuse freely at the surface the bubble would tend to become spherical. If, however, the number of diffusing atoms is limited - for example by a nucleation process - the faceted morphology would be retained even though an excess pressure exists. Hence a combination of thermodynamics and kinetics must be used to explain the morphological variations observed in Nb-1%Zr at 1050°C.

7.2 SHAPE CHANGES AT 1050°C

The faceted polyhedra, composed of 6 square \{100\} and 12 hexagonal \{110\}, observed up to 8 hours have the morphology indicated by the details of a polar surface energy $\gamma$-plot (175). These bubbles are close to satisfying the equilibrium conditions set out in equations 7.1 and 7.2, but it will be shown below that even this general morphology may contain a slight excess gas pressure. The vacancy concentration is high during short anneals because of the extra numbers introduced by implantation. The displacement damage values given in Table 9 suggest that the maximum implantation-induced concentration, $C^v$, is $\sim 10^{-2}$ or $10^{-3}$. This is low compared to the damage inflicted by heavy ions or neutrons, but still higher than the 1050°C thermal equilibrium value of $10^{-12}$ which was calculated using the heat of vacancy formation estimated by Rantanen and Donaldson (49) - i.e. 297 kJ/mole. During the early stages of annealing many vacancies recombine with self-interstitials, and many are consumed by bubble nucleation, but thereafter the number available to equilibrate a bubble after coalescence rapidly diminishes with increasing time. Thus after prolonged annealing the vacancy concentration will be reduced to near the thermal equilibrium level.

If a bubble is truly at vacancy equilibrium - i.e. its gas pressure exactly balances the surface energy - it is possible to
estimate the surface energy ratio \( \gamma^{100}/\gamma^{110} \) by measuring the distance \( x \) between opposite \( \{100\} \) faces of the tetrakaidodecahedron, and \( y \) the side of the square \( \{110\} \) faces. These measurements are related to \( \gamma^{100}/\gamma^{110} \) by the simple relationship (111):

\[
\frac{y}{x} = \sqrt{2} - \frac{\gamma^{100}}{\gamma^{110}} \quad \cdots (7.5)
\]

Nelson et al. (111) have used equation 7.5 to deduce a surface energy ratio of 1.14 from measurements of He bubbles formed in Mo after a 1 hour post-implantation anneal at 2000°C. Their bubbles had more developed \( \{110\} \) faces but were otherwise of identical shape to those described above for Nb-1%Zr. Equation 7.5 was applied to bubbles in Nb-1%Zr which had been annealed for 8 hours at 1050°C. It was not possible to accurately measure the smaller bubbles but analysis of 40 of the larger ones (see, for example, figure 15a) revealed a \( \gamma^{100}/\gamma^{110} \) of 0.96. Intuitively one would expect a ratio greater than unity if the close-packed (110) plane in b.c.c. metals has the lowest energy. The data of Zaremba (176), who has correlated surface energy with elastic and optical properties, suggests that \( \gamma^{100}/\gamma^{110} \) would be 1.097 for Nb. However, the experimental ratio of 0.96 -- which implies that \( \gamma^{100} < \gamma^{110} \) in Nb-1%Zr if the bubbles satisfy the conditions of equations 7.1 and 7.2 -- can be explained by investigating the coalescence phenomenon.

Bubble coalescence consists of two stages namely a) surface re-arrangement after collision, and b) volume adjustment by vacancy absorption to relieve the excess pressure (86). The results in chapter 6 for Nb-1%Zr at 1050°C imply that the nucleation of atomic ledges on bubble facets will limit the surface diffusion process (more quantitative verification of this is presented in due course), however, facet areas are small for short anneals, and so the small critical step size is unlikely to impose much of a restriction on the shape re-arrangement process. Volume adjustment, however,
requires long-range transport of vacancies whose matrix supersaturation is rapidly depleted during annealing. Thus equilibration of the excess pressure will undoubtedly be the slowest process - see section 7.4. The $\{100\}/\{110\}$ polyhedra in Nb-1%Zr may well contain a slight over-pressure even though their general shape is that expected for true equilibrium.

If this is so, the bubble will minimize the associated strain energy by developing higher energy planes in accordance with equation 7.3. The easiest way to do this is to develop $\{100\}$ faces at the expense of the $\{110\}$, and consequently $J^{100}/J^{110}$ will be reduced below unity depending on the extent of the over-pressure. The appearance of $\{100\}$ cubes during intermediate and longer anneals is explained merely by an extension of the argument. For long anneals the vacancy concentration is near to the thermal equilibrium level and so the excess pressure caused by subsequent coalescences will not be totally relieved. When the excess pressure is sufficiently great the $\{110\}$ faces will be eliminated in preference to the $\{100\}$ which minimize the associated strain energy and produce a cubic morphology.

The development of a cubic shape bounded by $\{100\}$ may seem contrary to the conclusion of Nelson et al. (111) that over-pressurized bubbles would tend to a spherical shape. Since the bubble volume is initially conserved on coalescence, it is interesting to compare the surface energies of a sphere, radius $r$, and a cube of identical volume. The sphere provides a surface energy of $12.57r^2\gamma_{\text{random}}$ to oppose the gas pressure within the bubble, whereas a cube provides $15.59r^2\gamma^{100}$. Thus $\gamma^{100}$ may be up to 20% lower than $\gamma_{\text{random}}$ and still supply the same total surface energy. It does not seem improbable, therefore, that cubic bubbles develop in response to an excess pressure.

7.3 ELONGATED AND STEPPED BUBBLES

To explain the stepped, and $\{100\}$ brick-shaped bubbles which were frequently observed in samples annealed beyond 25 hours, it is necessary to consider the
post-coalescence shape re-arrangement mechanism in more detail. These bubbles clearly do not represent the minimum surface energy per unit volume and so their presence implies that shape equilibration is limited by factors apart from simple surface diffusion. The kinetic and thermodynamic properties of crystal surfaces have been discussed by Hirth (177) and Gjostein (178, 179) and extensively reviewed by Neumann and Neumann (180), while Burton et al. (181) have studied the growth of a crystal surface normal to itself. Surface diffusion, which can be considered in terms of the Terrace-Ledge-Kink model illustrated in figure 37, is described by the Arrhenius equation:

\[ D_s = D_0 \exp \left( -\frac{Q_s}{RT} \right) \]

where \( D_0 \) is related to the frequency with which an atom leaves a ledge, and \( Q_s \) is a combination of the energies required to produce ad-atoms from the ledge, and to move them over the surface.

Willertz and Shewmon (110) have pointed out that bubble facets are likely to be atomically smooth, and so these ledges must first be nucleated by re-arranging surface vacancies (see figure 37) into the required stable configuration. If this ledge nucleation process occurs infrequently then bubble mobility, and shape re-arrangement after coalescence, will be very slow. The experimental results in Chapter 6 suggest that this nucleation process limits the mobility of He bubbles in Nb-1%Zr at 1050°C. It is, therefore, of interest to investigate post-coalescence shape re-arrangement limited by surface diffusion, and step nucleation, so that the conditions for which each is limiting in this material can be quantified.

Consider a 'brick-shaped' \{100\} bubble which has edge dimensions \( a, b, \) and \( c \), such that \( a \neq b \neq c \) (figure 38). In the absence of a bulk vacancy flux face 3 in figure 38 can only move if atoms are transferred from faces 1 and 2. Equivalently, face 6 can be considered to migrate by the
Figure 37: The Terrace-Ledge-Kink model of a surface 
(after Neumann and Neumann (1980))

Figure 38: A) Schematic brick-shaped bubble bounded 
by \{100\}
B) The critical nucleus size on face 1,
transfer of atoms from faces 4 and 5. Consequently, the total bubble volume is conserved (86) as the shape reverts to the \{100\} cubic morphology to minimize the surface energy per unit volume. The whole shape re-arrangement process is limited by the rate at which atoms leave faces 1 and 4, and so a comparison of the velocity of face 1, for example, normal to itself when a) ledge nucleation, and b) surface diffusion, is limiting, provides information on the most likely control mechanism in Nb-1\%Zr.

Consider firstly the velocity, $V_n$, of face 1 when ledge nucleation is limiting. Initially surface vacancies must be arranged in a stable configuration to produce a hole bounded by a ledge. This hole may be a 'pillbox' nucleated at the centre of the face (110), or alternatively, a quadrant emerging from a facet corner in an analogous manner to that described by Beeré and Reynolds (119). The latter is generally the lower energy configuration, and so the activation energy to form a hole emerging from a corner on face 1 is (119)

$$\Delta G = L\varepsilon + \frac{L^2h\Delta G_v}{\pi} \quad \ldots \ldots (7.6)$$

Here $L$ and $h$ are the length and height, respectively, of the ledge surrounding the nucleus, $\varepsilon$ is the ledge energy per unit length, and $\Delta G_v$ is the Gibbs free energy change per unit volume of nucleus. Hirth and Pound (182) have reviewed the nucleation of holes in flat surfaces, and describe $\Delta G_v$ as

$$\Delta G_v = -\frac{kT}{\Omega} \ln \frac{N}{N_e}$$

where $N$ is the actual number of vacancies in the surface, and $N_e$ is the equilibrium number at temperature T. It was noted earlier that stepped and truncated bubbles were most often observed after long anneals. The bulk vacancy concentration is close to the thermal equilibrium level for these anneals, and so to a first approximation $N = N_e$ and $\Delta G_v = 0$.

The second term in equation 7.6 is zero.
and so the activation energy $\Delta G^*$ to produce a hole bounded by a ledge of critical size $L^*$, is (110)

$$\Delta G^* = L^* \varepsilon$$

The critical size $L^*$ is defined by the hole which encompasses the minimum dimension of face 1 as shown schematically in figure 38 b). Once a ledge has reached this size it will readily reduce its total line energy by extending along the length of the face. The nucleation frequency of critical size ledges on face 1 is given by (110):

$$f(1) = \frac{2D_s L^*}{a_s h} \exp \left( - \frac{\Delta G^*}{kT} \right) \ldots \ldots \ldots \ldots \ldots (7.7)$$

where $D_s$ is the surface diffusion coefficient, and $a_s$ is the mean atomic jump distance. Figure 38 b) reveals that for face 1 $L^* \approx \pi b/2$, and so equation 7.7 reduces to

$$f(1) = \frac{D_s \pi b}{a_s h^2} \exp \left( - \frac{\pi b \varepsilon}{2kT} \right)$$

Since $V_n = f(1) h$, the normal velocity of face 1 if ledge nucleation is limiting atomic transport is described by:

$$V_n = \frac{D_s \pi b}{a_s h} \exp \left( - \frac{\pi b \varepsilon}{2kT} \right) \ldots \ldots \ldots \ldots \ldots (7.8)$$

In order to derive an equivalent expression for $V_d$ - the velocity of face 1 when surface diffusion is limiting - it is assumed that diffusing atoms on face 1 are only transferred to face 3. Although this neglects any atomic fluxes to other faces, it is unlikely to introduce major errors to the analysis which can also be performed on these faces separately. When material is transferred from face 1 the bubble dimension $a$ in figure 38a) is reduced by $da$, and $c$ increases by $dc$. If second order terms are neglected, and the bubble volume is conserved, it can easily be shown that the energy change per unit volume of material transferred from
face 1 is (119):
\[-2\gamma(a - c)\]
\[\frac{ac}{\gamma}\]

Since energy is needed to remove atoms from face 1, and also to nucleate fresh atomic planes on face 3, the average driving force for the diffusion of atoms from face 1 is approximately half the total energy change given above, ie.
\[\Delta G_{\nu}^{13} = -\gamma(a - c) \frac{ac}{\gamma} \ldots \ldots \ldots (7.9)\]

Shevmon (183) has given the surface diffusion flux as
\[J_s = -D_s \frac{d\mu}{kT\Omega} dx\]

where \(\Omega\) is the atomic volume, and \(d\mu/dx\) is the chemical potential change with distance in the surface. For a flux of atoms from face 1 to face 3
\[\frac{1}{\Omega} \frac{d\mu}{dx} \int \frac{\Delta G_{\nu}^{13}}{a} dx\]

and, therefore,
\[J_s = -D_s \frac{\Delta G_{\nu}^{13}}{akT} \ldots \ldots (7.10)\]

The number of atoms moving from face 1 to face 2 through an area \(bh\), is \(J_s bh\). (Here \(h\) is the thickness of the diffusion layer on face 1, and is approximately the same as the ledge height in equation 7.8). It will take time \(t = (abh)/(\Omega J_s bh)\) to empty face 1 to a depth \(h\), and so the normal velocity is
\[V_d = \frac{h}{t} = \frac{J_s \Omega h}{a}\]

Substituting equation 7.10 provides:
\[V_d = -D_s \frac{\Omega h \Delta G_{\nu}^{13}}{a^2kT} \ldots \ldots (7.11)\]

The most convenient way of analysing the contributions of surface diffusion and ledge nucleation to the shape changing
process is via the ratio \( \frac{V_n}{V_d} \) which equations 7.8 and 7.11 provide as:

\[
\frac{V_n}{V_d} = - \frac{2 \pi b \ln \Omega}{a_s^2 \Omega \Delta \lambda} \exp \left( \frac{\pi b \epsilon}{h \Delta \lambda} \right) \quad \text{(7.12)}
\]

It is clear that \( \frac{V_n}{V_d} \) is dependent not only on the edge energy \( \epsilon \), which is a fundamental parameter of the bubble surface, but also on the actual bubble dimensions \( a, b, \) and \( c \). Take, for example, a brick-shaped bubble with \( a = 8 \) nm, \( b = 4 \) nm, and \( c = 4 \) nm. If \( \gamma = 1500 \) mJ/m\(^2\), \( a_s = 1 \) nm, \( \Omega = 1.79 \times 10^{-29} \) m\(^3\), \( T = 1323 \) K, and \( h = 0.165 \) nm, then \( \frac{V_n}{V_d} = 1 \) when \( \epsilon = 3.49 \times 10^{-11} \) J/m, and ledge nucleation will limit shape re-arrangement for \( \epsilon > 3.49 \times 10^{-11} \) J/m.

Similarly, if the bubble is even more truncated with \( a = 16 \) nm, \( b = 4 \) nm, and \( c = 4 \) nm, ledge nucleation will again be limiting for \( \epsilon > 3.77 \times 10^{-11} \) J/m. However, in general \( a \neq b \neq c \) and if, for example, the bubble is a flat slab with \( a = 16 \) nm, \( b = 12 \) nm, and \( c = 4 \) nm, then ledge nucleation is limiting for \( \epsilon > 1.36 \times 10^{-11} \) J/m. This variation of the limiting \( \epsilon \) value with the actual bubble morphology occurs because the dimension \( 'b' \) appears inside the exponential term in equation 7.12.

It is shown in chapter 8 that \( \epsilon \) in Nb-1\%Zr after long anneals at 1050°C is \( 4.3 \times 10^{-11} \) J/m, although this value is much higher (\( 1.1 \times 10^{-10} \) J/m) at shorter times. For the morphologies and bubble sizes above, which are similar to those in Nb-1\%Zr beyond 25 hours, these edge energies indicate that ledge nucleation always limits shape re-arrangement and, therefore, bubble mobility. For example, if \( a = 8 \) nm, \( b = 4 \) nm, \( c = 4 \) nm, and \( \epsilon = 4.3 \times 10^{-11} \) J/m, equation 7.12 reveals that the velocity of face 1 is \( \approx 17 \) times slower than if surface-diffusion were the limiting mechanism. Clearly the many bubbles exhibiting non-equilibrium shapes in this material do so as a consequence of the ledge nucleation limited kinetics. The surface steps and more irregular shapes are most likely to occur as a result of a) bubble collisions in directions apart from \( \langle 100 \rangle \), and b) both single and multiple collisions between large and smaller bubbles.
In Nb at the same temperature He bubbles are larger than in the alloy and grow initially by surface diffusion limited migration and coalescence (96). However, when the characteristic bubble size reaches approximately 16 nm - i.e. beyond 25 hours at temperature - the kinetics apparently change to ledge nucleation control with $\varepsilon_{\text{Nb}}$ deduced to be $\approx 1.5 \times 10^{-11} \text{J/m}$ (see chapter 8 section 8.1). Shape re-arrangement should, therefore, be surface diffusion limited initially, but ledge nucleation limited for times in excess of 25 hours. If two 16 nm bubbles collide to produce a brick-shaped morphology with $a = 32$ nm, $b = 16$ nm, and $c = 16$ nm, then equation 7.12 predicts that ledge nucleation will be limiting provided $\varepsilon > 1.27 \times 10^{-11} \text{J/m}$. Since $\varepsilon_{\text{Nb}} > 1.27 \times 10^{-11} \text{J/m}$, then ledge nucleation limited mobility and post-collision shape re-arrangement is clearly feasible for bubbles of this size and morphology in pure Nb. Although the actual mechanism limiting shape changes is dependent on both $\varepsilon$ and the non-equilibrium bubble morphology, the simple analysis presented in this section does demonstrate that the presence of irregular bubbles, in Nb-1%Zr particularly, can be explained if the nucleation of atomic ledges on bubble facets is difficult.

7.4 THE VACANCY FLOW TO EQUILIBRATE BUBBLES

An essential feature of the arguments presented in section 7.2 to explain the development of $\{100\}$ cubes in Nb-1%Zr at $1050^\circ\text{C}$, was that bubbles do not achieve vacancy equilibrium and so contain an excess pressure. To obtain some semi-quantitative evidence for this, the rate of change of bubble size by vacancy flow can be considered using an equation similar to that originally derived by Greenwood et al. (56) for spherical bubbles. It was deduced that the growth rate of a spherical bubble, radius $r$, containing a pressure $P$, in the presence of a thermal equilibrium vacancy concentration $c_e^V$, would be given by equation 7.13 where $D_v^V$ is the vacancy diffusion coefficient, $\Omega$ is the atomic volume, and $\varepsilon$ is the surface energy. The term $(P - 2\varepsilon/r)$
represents the excess pressure within the bubble.

\[ \frac{dr}{dt} = \frac{D_v C_e \Omega}{r kT} (P - \frac{3\gamma}{r}) \quad \ldots \ldots (7.13) \]

If a similar derivation is performed for a cubic bubble, equation (7.13) is only modified by the replacement of \( r \) with \( a/2 \), where \( a \) is the cube edge length.

Equation 7.13, with \( r = a/2 \), can now be used to estimate the time needed to relieve an arbitrary excess pressure. Rantanen and Donaldson (49) have deduced that the heat of formation of a vacancy in Nb is 297 kJ/mole, and so \( C_e \) at 1050°C will be \(~10^{-12}\). However, if the matrix vacancy supersaturation is only reduced to \(~10^{-9}\) during annealing, and \( D_v \) is considered to be \(~10^{-19}\) m²/sec (slightly faster than the Nb self-diffusion coefficient of \( 9 \times 10^{-21}\) m²/sec at 1050°C (184)), then the shortest feasible time for equilibration can be estimated. Hence for \( \Omega = 1.79 \times 10^{-29}\) m³, and \( T = 1323\) K, the time required for a bubble to grow from 5.0 to 5.05 nm to relieve an over-pressure of 10 MN/m² would be \(~10^{11}\) seconds. Even if the excess pressure is \(~10^{3}\) MN/m² the time necessary is still \(~10^9\) seconds, and so bubbles will be over-pressurized for a significant time if the vacancy concentration is at, or close to, the thermal equilibrium level.

It is possible to demonstrate experimentally that bubbles are over-pressurized by introducing more vacancies to a bubble population which was produced by a long anneal. These vacancies will be absorbed by bubbles and the flux will significantly disturb the surface so that faster shape rearrangement is possible. Consequently, bubbles should become rounded as they minimize their strain energy per unit volume in accordance with equation 7.3. Eventually, if enough vacancies are available, bubbles will regain their faceted morphologies as they equilibrate to the conditions given in equations 7.1 and 7.2. To illustrate experimentally that bubbles in Nb-1%Zr do contain an excess pressure a population of non-equilibrium bubbles produced by 70 hours growth at 1050°C...
FIGURE 39: Demonstration of excess pressures inside bubbles in Nb-1%Zr after 70 hours at 1050°C.

a) Typical bubble morphologies after 70 hours at 1050°C (close to [100] beam direction).

b) & c) Spheroidized bubbles after reannealing a) at 1350°C for 1 hour ([100] and [111] directions, respectively).

d) Faceted bubbles grown for 2 hours at 1350°C ([111] beam direction).
shown in figure 39a - was reannealed under UHV conditions for 1 hour at 1350°C. This treatment produces a thermal equilibrium vacancy concentration which is two orders of magnitude higher, and also increases the vacancy mobility. The bubbles become distinctly rounded (Figures 39b and 39c) whereas bubbles which have been grown specifically at 1350°C are crisply faceted (Figure 39d). The bubbles in Nb-1%Zr after prolonged anneals at 1050°C must clearly contain an excess pressure.

7.5 SUMMARY

Bubble shape changes in Nb-1%Zr during annealing at 1050°C can be explained in terms of the competition between thermodynamic requirements and kinetics. The \{110\}/\{100\} polyhedra observed predominantly at short times are close to the equilibrium morphology, and their volume adjustment is relatively easy due to the high matrix vacancy concentration provided by the initial implantation process. However, this high initial vacancy supersaturation is not replenished during annealing but is reduced to approximately the thermal equilibrium level. Consequently bubbles produced by intermediate or long anneals do not equilibrate their volume after coalescence and so become over-pressurized. The bubbles try to adjust to the thermodynamic conditions given by equation 7.3, but the shape rearrangement process after coalescence is slow because ledge nucleation is limiting for most non-equilibrium bubble morphologies. Hence, as the annealing time increases there is a greater tendency for bubbles to contain an excess pressure, and many will exhibit irregular, non-equilibrium, morphologies.
8.1 BUBBLE GROWTH MECHANISMS

In Chapter 6 it was asserted that the bubble size variation with annealing time for Nb-0.3 and 2.07% Zr at 1050°C, and Nb-1.0% Zr at 950, 1050, and 1250°C, was indicative of a migration and coalescence growth mode limited by step nucleation (regardless of the presence of two saturated sizes in Nb-0.3% Zr and Nb-1.0% Zr at 1050°C). To quantify this reasoning, and to deduce the role of Zr in these materials, it is essential to rigorously investigate the growth process in pure Niobium. Aitken (96) has found that He bubbles in Nb containing 400 wt.ppm O grow by migration and coalescence limited by surface diffusion at 950, 1050, and 1250°C. Bubbles in this material were again essentially 100 cubes and so his results - which are converted to be compatible with the Nb-Zr data - are summarized in table 15.

The pure Nb data in table 15 is compared to the equivalent results for the Nb-Zr materials in the Log (size) vs. Log (time) plots shown in figure 40 a), b), and c). It is readily apparent that bubbles in the Nb-Zr alloys at 950, and 1050°C - figures 40 a) and b), respectively - are significantly smaller than their counterparts in Nb. A re-analysis of a Nb sample produced after 1 hour at 1050°C provided a bubble density of \(8 \times 10^{21} \text{ m}^{-3}\), whereas the Nb-Zr alloys having received the same treatment yielded densities between \(3 \times 10^{21}\) and \(7 \times 10^{22} \text{ m}^{-3}\). Hence although Zr additions reduce the characteristic bubble size the cavity density increases by a factor of approximately 6 or 7. However, at 1250°C - figure 40 c) - bubbles in Nb-1.0% Zr are initially smaller than those in Nb, but the break-away phenomenon occurring after 2 hours at temperature increases bubble size to about 4 times that of the pure Nb dimension, within 40 hours.

Aitken (96) found that the least-squares slopes of his data corresponded to a surface diffusion limited,
<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>Annealing time (hours)</th>
<th>Characteristic cube size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>$\frac{1}{4}$</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2}$</td>
<td>5.6</td>
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<td>9.9</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>13.7</td>
</tr>
<tr>
<td>1050</td>
<td>$\frac{1}{4}$</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
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<td>17.2</td>
</tr>
<tr>
<td>1250</td>
<td>$\frac{1}{4}$</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>$\frac{1}{2}$</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>1</td>
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</tr>
<tr>
<td></td>
<td>50 *</td>
<td>25.1</td>
</tr>
</tbody>
</table>

* Extra data provided by the present work

Table 15: The variation of bubble size with annealing time for Niobium containing 400 wt.ppm O (after Aitken (96)).
Cube size (nm)

Figure 40 a): 950°C
A comparison of Nb and Nb-1%Zr data.

Annealing time (hours)

Figure 40 b): 1050°C - A comparison of Nb and Nb-1%Zr data.

Annealing time (hours)
migration and coalescence growth mode. However, a careful examination of his 1050°C results - figure 40 b) - reveals that the bubble size curve flattens out for anneals beyond 10 hours. The presence of a terminal size in Nb, which was qualitatively noted by Johnson and Cost (121), has been verified for the higher temperature of 1250°C by the production of extra data at 25 and 50 hours. These findings indicate that the kinetics limiting bubble mobility at some point change from surface diffusion to facet nucleation. The relative bubble mobilities based on each of these rate-controlling mechanisms can be expressed as the ratio:

\[ R = \frac{D_b^{(\text{facet nucleation})}}{D_b^{(\text{surface diffusion})}} \]  \hspace{1cm} (8.1)

\( D_b^{(\text{facet nucleation})} \) and \( D_b^{(\text{surface diffusion})} \) are derived for cubic bubbles in the Appendices, and their substitution into equation (8.1) results in an expression for \( R \) which is
independent of the surface diffusion coefficient $D_s$, i.e.

$$R = \frac{\pi a_s^5}{2 h Q} \exp - \frac{a \mu \epsilon}{2 kT} \quad \ldots \ldots (8.2)$$

Here $\Omega$ is the atomic volume $= 1.79 \times 10^{-29} \text{ m}^3$, $a_s$ is the average jump distance of an ad-atom on the surface (assumed to be $\approx 1.0 \text{ nm}$ for all the annealing temperatures since they are $0.55T_m$ or below), $a$ the bubble cube dimension; and $\epsilon$ the edge energy per unit length of step at the bubble surface.

When surface diffusion makes way for step nucleation $R = 1$ and equation (8.2) can be used to deduce $\epsilon$ for a Niobium (100) surface. The bubble size at which the kinetics change is, according to Table 15, $\approx 16.2 \text{ nm}$ at 1050°C, and 23.5 nm at 1250°C. The substitution of these sizes with the other parameters described above provides $\epsilon = 1.43 \times 10^{-11} \text{ J/m}$ at 1050°C, and $\epsilon = 1.24 \times 10^{-11} \text{ J/m}$ at 1250°C.

These values are within the range of $10^{-11}$ to $10^{-10} \text{ J/m}$ found for Cu and Au (185), and a 'broken-bond' estimate based on $\gamma_{100} \approx 1500 \text{ mJ/m}^2$ provides an answer of the same magnitude. However, to justify the assumption that the flattened portions of the Nb results correspond to step-nucleation limited migration and coalescence, the data must be quantified in terms of the growth equations for {100} cubes derived in Appendix I and II.

Equation (AII.11), which describes surface diffusion limited migration and coalescence, was applied to the Nb data to deduce the surface diffusion coefficient, $D_s$, at each temperature. The values assigned to the other relevant parameters are given in Table 16. The variation of $a_s$ with temperature is largely unknown and so it was assumed to be constant for all temperatures up to 1250°C (which represents only $0.55T_m$). The $D_s$ values which provided the best fit to the surface diffusion portion of the results were $4.4 \times 10^{-14} \text{ m}^2/\text{sec}$ at 950°C, $5.8 \times 10^{-13} \text{ m}^2/\text{sec}$, and $3.0 \times 10^{-11} \text{ m}^2/\text{sec}$, at 950, 1050, and 1250°C respectively. The relevant $D_s$ was then used in equation (AII.5), which describes migration and coalescence limited by step nucleation, together with the values in Table 16 to
match the saturated sizes in Nb at 1050 and 1250°C. The best fit was obtained for $\varepsilon = 1.5 \times 10^{-11}$ J/m at 1050°C, and $\varepsilon = 1.4 \times 10^{-11}$ J/m at 1250°C. These are in excellent agreement with those values derived from the ratio of the bubble mobilities - equation (8.2).

The match between the experimental data and the theoretical predictions for Nb at 1050°C is demonstrated by Figure 41, which also illustrates the main features of the facet nucleation limited growth mechanism specified by equation (AII.5). The slope of this curve is $\sim 0.05$ (although it gradually diminishes with increasing time) in accordance with the findings of other workers with different bubble morphologies (110, 113). The methods applied above can now be used to investigate the experimental data for the Nb-Zr alloys. In all of these materials there is no reliable evidence for an initial period of surface diffusion limited mobility, and so $\varepsilon$ cannot be found directly using the $D_b$ ratio of equation (8.2). However, we can say that $R < 1$ for the initial size plateaux in Nb-0.3%Zr at 1050°C and Nb-1%Zr at 950, 1050, and 1250°C, and solve equation (8.2) as an inequality to deduce the likely limits of $\varepsilon$. These results, assuming the $\Omega$ and $a_s$ values given in Table 16, are summarized in Table 17.

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
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<tr>
<td>$\Omega$</td>
<td>$1.79 \times 10^{-29}$ m$^3$</td>
</tr>
<tr>
<td>$b$</td>
<td>$4.48 \times 10^{-29}$ m$^2$ (REF: 186)</td>
</tr>
<tr>
<td>$z$</td>
<td>0.1 (see REF: 121)</td>
</tr>
<tr>
<td>$m$</td>
<td>$5 \times 10^{-26}$ He/m$^3$</td>
</tr>
<tr>
<td>$\gamma^{100}$</td>
<td>1500 mJ/m$^2$</td>
</tr>
<tr>
<td>$a_s$</td>
<td>1.0 nm</td>
</tr>
</tbody>
</table>

Table 16: Values of parameters used in conjunction with equations (AII.11) and (AII.5) to match the Nb data at 950, 1050, and 1250°C.
Figure 41: The matched Nb and Nb-1%Zr data at 1050°C.
To apply the facet nucleation growth equation - equation AII.5 - to the alloy data a value for $D_s$ must be known for each temperature and composition. However, in the absence of more specific data $D_s$ was assumed to be the same as the Nb values given previously, i.e. $4.4 \times 10^{-14}$, $5.8 \times 10^{-13}$, and $3.0 \times 10^{-11} \text{m}^2/\text{sec}$ at 950, 1050, and 1250°C respectively. Within this assumption, and using the parameters given in Table 16, equation (AII.5) was used to match all size plateaux in the alloys. The best-fit edge energies are summarized in Table 17 above, and the correlation between the experimental data and the prediction of equation (AII.5) is illustrated for Nb-1%Zr at 1050°C in Figure 41.

The $\varepsilon$ values derived from equation (AII.5) agree well with the conditions deduced from the $D_b$ ratio, and it is clear that Zr additions of up to 1% not only progressively reduce bubble size, but also increase $\varepsilon$ by a factor between 5 and 8 at 1050°C. The presence of a second terminal size in Nb containing 0.3 and 1%Zr at this temperature (see figure 40b).
implies that $\xi$ has reduced subsequently to the level found for Nb-2.07%Zr - i.e. $4.3 \times 10^{-11}$ J/m. The reasons for, and the consequences of, such behaviour are discussed in section 8.3. The saturated size of bubbles in Nb-1%Zr at 1250°C extends only for anneals up to 1 hour but again $\xi$ is higher than at the same temperature in Niobium. The peculiar behaviour found for longer annealing times is also discussed in section 8.3.

In conclusion, therefore, it has been shown in this section that the presence of a terminal bubble size in Nb and Nb containing small quantities of Zr, is indeed indicative of a step nucleation limited migration and coalescence growth mode. Bubble growth in Nb at 1050°C and 1250°C exhibits a change in controlling kinetics from surface diffusion to ledge nucleation, whereas bubble mobility in the Nb-Zr alloys is always ledge nucleation limited. The particular influence of Zr has been quantified in terms of the edge energy, $\xi$, which is related to the composition and cleanliness of the bubble surface.

8.2 THE ROLE OF ZIRCONIUM

It was shown in the previous section that Zr increased the edge energy of Niobium at all temperatures, although the effect was particularly pronounced in Nb-0.3%Zr and Nb-1%Zr at 1050°C. This implies that the surface energy also increases when Zr is present. To verify this consider two bubbles, one in material $A$ and the other in material $B$, which contain the same number of gas atoms 'n' at temperature T. Assuming for simplicity that the gas behaves ideally, then $P_A V_A = nkT = P_B V_B$, i.e.

$$P_A V_A = P_B V_B$$

If the gas pressure balances the surface energy then $P_A = \frac{h \gamma^A}{a_A}$ and $P_B = \frac{h \gamma^B}{a_B}$, where $a_A$ denotes the bubble cube size. Simplification of equation (8.3) results in a straightforward relationship between the surface energies and the bubble sizes.
in the two materials ie.

\[
\frac{\gamma^A}{\gamma^B} = \left[ \frac{a_B}{a_A} \right]^2 \quad \ldots \ldots (8.4)
\]

If A denotes Nb and B corresponds to a Nb-Zr alloy having a higher surface energy, then \( \gamma^A/\gamma^B < 1 \) and therefore \( a_B \) must be smaller than \( a_A \). Thus any increase in surface energy should result in a smaller bubble size. This is clearly illustrated by the Log/Log plots for Nb containing up to 2.07% Zr at 1050°C - see figure 40 b).

In dilute alloys 'Gibbsian' (ie. reversible equilibrium) segregation tends to enrich the first few atomic layers of a surface with the component having the lowest surface energy \( \gamma^A \). The enrichment factor can be expressed as \( \gamma^A \):

\[
\frac{C^A}{C^B} = \exp \left( \frac{(\gamma^B - \gamma^A)}{RT} \right) \quad \ldots \ldots (8.5)
\]

where \( C^A \) and \( C^B \) are the solute concentrations in the surface and bulk respectively, \( Z \) is the average area occupied per mole of atoms, and \( \gamma^A \) and \( \gamma^B \) are the surface energies of the solute and solvent respectively. Zirconium has an average \( \gamma \) of \( \sim 1850 \) mJ/m\(^2\) compared to 2100 mJ/m\(^2\) for Nb \( (189) \) and so should enrich a bubble surface slightly. At 1050°C, and assuming \( Z = 5.4 \times 10^{-4} \) m\(^2\) (from the data in Ref. 188), equation (8.5) predicts the Zr concentration at a bubble surface in Nb-1%Zr to be 1.68%. Thus although this effect is small it does demonstrate that Zr would tend to decrease rather than increase \( \gamma \) and \( \varepsilon \). Simple solute - surface interactions therefore do not explain why \( \varepsilon \) should increase when 0.3 to 2.07% Zr is present. However, this phenomenon can be explained if the nature of solute - interstitial interactions are investigated, but first it is shown that bubble surfaces in Nb are likely to be heavily contaminated with O, N, and C.

The ability of Nb at elevated temperatures to retain large amounts of interstitial elements - particularly
Oxygen which has a solubility limit of \( \approx 5.5 \text{ at.\%} (1 \text{ wt.\%}) \) at \( 1100^\circ\text{C} \) is well-known. The segregation of O, N, and C, individually or collectively, may change the bubble surface characteristics by interfering with a) the surface diffusion process, and b) surface energy anisotropy which produces faceting on more than one plane. Investigations by Williams et al. \((190)\) have shown that O and N impurities in Nb diffuse and become trapped at damage introduced by neutron irradiation, provided the temperature is above \( \approx 150^\circ\text{C} \). Nolfi \((191)\) has shown that interstitial segregation during irradiation could be responsible for the ordered void arrays frequently observed in refractory metals. He proposed that these arrays form because the interaction energy of segregant-lined voids can be minimized with respect to their spacing. Some evidence for this is provided by Loomis et al. \((192)\) who found that the spacing of arrays in heavy-ion bombarded Nb and Nb-1\%Cr varied with O concentration. These changes agreed well with predictions based on Nolfi's theory, and O was deduced to segregate to void surfaces. It was suggested that this segregation arose from the intrinsic need to reduce the free energy of the Nb matrix rather than being a consequence of radiation alone.

A number of researchers have used Auger Electron Spectroscopy (AES) to study equilibrium surface segregation in Nb as a function of temperature and bulk O concentration. Hofmann et al. \((193)\) have shown that O covers in excess of 90\% of the surface at temperatures below \( 825^\circ\text{C} \), independent of the bulk O content. Segregation diminishes above this temperature dependent on the bulk O content, but surface coverages of 50\% or more remain at \( 1000^\circ\text{C} \) and \( 1250^\circ\text{C} \) for matrix concentrations of 0.097\% (\( \approx 173\text{ppm} \)) and 0.66 at.\% (1180 wt. ppm), respectively. Similar results are presented by Joshi and Strongin \((194)\) who also crudely estimated the surface energy reduction at \( 1250^\circ\text{K} \) to be \( \approx 197 \text{ mJ/m}^2 \) per atom percent of O. However, Eelsen and Regnier \((195)\) who investigated the effect of gases on the surface energy of Cu by monitoring the disappearance rate of isolated voids (which were produced by self-ion irradiation) during annealing, observed a more dramatic effect. An increase in bulk O content from 5 wt.ppm to 100 wt. ppm.
ppm was found to reduce the surface energy by 33\%, whereas He produced no change at all. If, therefore, bubble surfaces in Nb are contaminated with large quantities of O, Y and E may be significantly reduced compared with what might be expected for a truly clean surface. Equilibrium between bulk and surface is instantaneous above 800°C (194) because of the high O diffusivity in Nb. For example, at 1050°C \( D = 9.252 \times 10^{-11} \) \( m^2/\text{sec} \) (assuming \( D_0 = 1.7 \times 10^{-6} m^2/\text{sec} \) and \( Q = 108 \text{ kJ/mole} \) (196)) and so an O atom would take less than a second to diffuse 1\( \mu \)m in one dimension.

Much less is known about the surface segregation of C and N whose bulk solubilities in Nb are lower, but it is reasonable to assume that their behaviour will be similar to that of O. Apart from equilibrium segregation interstitials may be dragged to bubble surfaces if they interact with vacancies. It was shown in Chapter 7 section that volume adjustment to equilibrate the excess pressures created by coalescence would, in general, require a significant amount of time, and so vacancies will always be biased to bubbles throughout annealing. Mondino and Seeger (197) have suggested that diffusing N and C can be trapped by monovacancies not only in \( \alpha \)-Fe, but also in Nb, Ta, and V. If this is the case, and N, or C, monovacancy pairs exist in the temperature range 950 - 1250°C, then the vacancy current to bubbles could build up non-equilibrium interstitial levels at the surface.

From the discussion above it seems increasingly likely that bubble surfaces in Aitken's Nb samples are 'dirty', and consequently the \( E \) values calculated at 1050 and 1250°C in section 8.1 are probably lower than would be found for interstitial-free surfaces. More quantitative evidence that these surfaces are indeed 'dirty' is provided by the \( D_s \) values which gave the best match to the surface-diffusion limited growth curves at 950, 1050, and 1250°C. These are summarized in Figure 42 together with a plot of \( \ln(D_s) \) vs. 1/T. Although there are only three points the data produces a straight line whose least-squares intercept and slope give \( D_0 = 11.54 \times 10^{-4} m^2/\text{sec} \), and \( Q_s = 332.8 \text{ kJ/mole}, \) respectively.
Temperature | $D_s \text{m}^2/\text{sec}$
--- | ---
950°C | $4.4 \times 10^{-14}$
1050°C | $5.8 \times 10^{-13}$
1250°C | $3.0 \times 10^{-11}$

Figure 42: Arrhenius plot of $\ln (D_s)$ vs. $1/T$ for Nb (deduced from matching Aitkens data with equation (AI.11)).

Allen (198), using grain boundary grooving, found $D_o = 4.3 \times 10^{-5}$ m$^2$/sec and $Q_s = 194.2$ kJ/mole for the surface self-diffusion of Nb, and Odishariya (199) has obtained $Q_s = 229.7$ kJ/mole from field emission measurements. The large discrepancy between the activation energy deduced from figure 42 and those of Allen (198) and Odishariya (199) can be interpreted in terms of the cleanliness of bubble surfaces. Clum (200, 201) has shown using FEM techniques that $Q_s$ values for Nb are dependent on the level of bulk impurities. For Nb having 99.983% purity $Q_s$ was 105 kJ/mole, whereas for 99.97% purity $Q_s$ was 373.8 kJ/mole. Hence as the bulk impurity content rises, and more interstitials segregate to a surface, the activation energy for surface diffusion dramatically increases.
increases. This has also been observed for other refractory metals when FIM techniques have been applied in variable vacuum conditions. Table 18 below (after Vanselow (202)) clearly demonstrates that surface impurities on W and Ta significantly increase $Q_s$.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$Q_s$ (eV)</th>
<th>Vacuum (Torr)</th>
<th>Vacuum (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>3.1</td>
<td>$10^{-12}$</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>3.14</td>
<td>$10^{-9}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>$0_2$, $\theta = 0.5$ *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>$0_2$, $\theta = 1.0$ *</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.7</td>
<td>$C$, $\theta = 0.5 - 1$ *</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>2.03</td>
<td>$3 \times 10^{-10}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>2.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $\theta$ represents the proportion of a monolayer coverage.

Table 18: The variation of $Q_s$ for W and Ta with the presence of surface impurities (after Vanselow (202)).

In general, the surface diffusivity, $D_s$, may be enhanced or suppressed by impurities dependent on the material (179, 180). If the surface is characterized by the Terrace-Ledge-Kink model shown in figure 37, then $Q_s$ can be considered as the sum of the energies required to a) produce ad-atoms from ledges, and b) move these atoms over the surface. The increasing $Q_s$ values with increasing surface contamination may be explained if ledge atoms are pinned so that the energy required for a) is increased. Alternatively, the same effect can be envisaged in a simpler manner if the ledge is considered to move with a discrete velocity. The presence of large amounts of interstitials would tend to pin the ledge, or reduce its velocity. This can be interpreted in terms of an increased $Q_s$. 

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However, it is clear from the discussion so far that the bubble surfaces in Aitken's Nb samples are contaminated with interstitials which have segregated from the bulk. Oxygen, with its bulk concentration of 400 wt.ppm, is likely to be the major contaminant although N and C may well be more surface active due to their lower matrix solubility. It is feasible, therefore, that the $\varepsilon$ values of $1.5 \times 10^{-11}$ and $1.4 \times 10^{-11}$ J/m at 1050 and 1250°C, respectively, are lower than would be provided by an interstitial-free Nb surface.

It is now possible to deduce why the presence of small amounts of Zr in Nb apparently increases $\varepsilon$ and also the edge energy $\varepsilon$. To explain this phenomenon due consideration of interstitial - solute interactions is essential. Bunn et al. (203) have performed internal friction experiments with Nb-0.9%Zr containing 50 to 3500 wt.ppm O, and Thurber et al. (204) have investigated Nb-1%Zr containing 3100 wt.ppm O and 120 wt.ppm N in the same manner. These researchers found that the normal Nb-O and Nb-N relaxation peaks were dramatically reduced in height, and new peaks due to Zr - interstitial interactions were observed at higher temperatures in the spectrum. These peaks were mainly caused by Zr-O interactions although a Zr-N peak was present if the O concentration was smaller than 1000 wt.ppm (203). Furthermore it was concluded that alloys containing less than 700 wt.ppm O had all of the O and part of the N associated with Zr atoms.

A more detailed internal friction investigation is reported by Miner et al. (205) for three Nb-1%Zr single crystals (100, 110, and 111) containing from 15 to 5300 wt.ppm O. A digital computer was used to identify three additional peaks, and the composition and orientation dependence of the peak heights indicated that they arose from 1) single O atoms, 2) N atoms on nearest-neighbour octahedral sites to Zr, and 3) a pair of O atoms on opposite nearest-neighbour sites around Zr atoms. A systematic study of substitutional solute - interstitial interactions in Nb performed by Szkopec and Ahmad (206) perhaps demonstrates best the internal gettering ability of Zr. They show that increasing the Zr concentration from 0.82% to 2.04%, whilst keeping the
interstitial content approximately constant (∼750 wt.ppm), causes a progressive reduction in the normal Nb-O and Nb-N relaxation peaks after the initial dramatic reduction produced by 0.82% Zr. In keeping with Dunn et al. (203), Zr was concluded to produce practically complete removal of O and N from free solid solution.

Further evidence of Zirconium's gettering ability is supplied by Perkins and Padgett (207) who have measured the diffusivity of O in Nb and Nb-Zr alloys (≤1% Zr) in the temperature range 550 to 1100°C. Their results show that at 1050°C, for example, the oxygen diffusivity is reduced by a factor of 3.4, and 7 in Nb containing 0.5, 0.8, and 1.0% Zr, respectively. Nitrogen diffusivity is also expected to be decreased by the presence of Zr (208). This affinity for O particularly has been employed by Pellog (209) to demonstrate that some of the anomalous self-diffusion data for Vanadium can be attributed to the influence of O impurities.

Unfortunately the interstitial contents of the Nb-0.3% Zr and Nb-1% Zr used in the present work, are unknown, but it seems reasonable to expect similar levels to those present in Nb-2.07% Zr, i.e. ∼600 wt.ppm O and ∼100 wt.ppm N. Accordingly, the interstitials in these materials should be almost totally associated with Zr, especially in the Nb-1% Zr alloy (203, 206), and consequently bubble surfaces will be cleaner than those in Nb because the contaminants are trapped in the bulk and also localized around Zr atoms in the surface. Thus, the increased values in Table 17 are probably more indicative of a true Nb surface, because of the cleansing effect of the small amount of Zr, than those values derived from Aitken's results in section 8.1. The fact that ε increases from 6.3 x 10⁻¹¹ J/m to 1.1 x 10⁻¹⁰ J/m at 1050°C when the Zr content increases from 0.3 to 1% - as derived from the reduction in size of the first plateau in figure 36 - suggests that Zr at the former level is insufficient to completely mop up all the interstitials.

To provide more quantitative evidence for this surface cleansing hypothesis, D₀, and an activation energy Qs for Nb surface diffusion have been derived from Nb-1% Zr data in the temperature range 900 to 1250°C. Samples were annealed
for 2 hours at each temperature within the range, and the modal cube dimension was deduced from measurements of 500 bubbles. The application of equation (AII.5) to the Nb-1%Zr results in figure 40b has shown that bubbles grow by facet nucleation-limited migration and coalescence in this temperature regime. The second term on the left-hand side of equation (AII.5) is small compared to the exponential term and so to a first approximation can be ignored. The equation can then be reduced to:

\[
\begin{align*}
\left[ \ln \left( \frac{T(aA + 3b)}{(aA + 2b)^2} \right) + \frac{\pi a \varepsilon}{2kT} \right] & \approx \ln \frac{\pi^2 zmd \sigma}{6 \varepsilon} - \frac{Q_s}{RT} \\
\end{align*}
\]

where \( \Lambda = kT/2 \gamma \), \( b \) is Van der Waals constant, and \( a \) is the characteristic cube dimension. Thus a plot of \( \gamma \) vs. \( 1/T \) yields \( Q_s \) from the slope and \( D_0 \) from the intercept provided \( \varepsilon \) and \( a_s \) are constant over the temperature range of interest.

At 950 and 1050°C equation (AII.5) - with \( D_s \) provided by the relevant Nb experimental value - provided edge energies of \( \sim 1 \times 10^{-10} \) J/m, but bubbles after 2 hours at 1250°C fall on the 'breakaway' portion of the growth curve (see figure 40c) where equation (AII.5) is inapplicable. The edge energy in equation 8.6 was assumed to be \( \sim 1 \times 10^{-10} \) J/m but obviously this is unreliable for the higher temperatures in the range. The experimental cube dimensions and \( \gamma \) values as a function of temperature are summarized in Table 19, and \( \gamma \) is plotted against \( 1/T \) in figure 43. This figure exhibits two linear portions having vastly different slopes. The first, which occurs above 1150°C (ie. \( 1/T < 7 \times 10^{-4} \)), has the greatest slope and yields \( Q_s = 4.7 \) MJ/mole which is clearly not feasible, and so demonstrates that \( \varepsilon = 1 \times 10^{-10} \) J/m is invalid above this temperature. For example, a more reasonable value for \( \varepsilon \) at 1250°C would be \( 6.0 \times 10^{-11} \) J/m (from Table 17) which reduces \( \gamma \) from 106.253 to 86.543 and therefore reduces the slope dramatically. However, the linear portion below 1150°C (ie. \( 1/T > 7 \times 10^{-4} \)) suggests that \( \varepsilon \) hardly deviates from

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Figure 43: The plot of $Y$ vs. $1/T$ for Nb-1%Zr in the range 900 to 1250°C

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$\frac{1}{T} \times 10^{-4}$</th>
<th>Cube dimension (nm)</th>
<th>$Y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>8.520</td>
<td>1.9</td>
<td>76.244</td>
</tr>
<tr>
<td>950</td>
<td>8.176</td>
<td>2.1</td>
<td>77.505</td>
</tr>
<tr>
<td>1050</td>
<td>7.558</td>
<td>2.3</td>
<td>77.871</td>
</tr>
<tr>
<td>1150</td>
<td>7.027</td>
<td>2.7</td>
<td>79.872</td>
</tr>
<tr>
<td>1200</td>
<td>6.788</td>
<td>5.2</td>
<td>91.957</td>
</tr>
<tr>
<td>1250</td>
<td>6.566</td>
<td>6.5</td>
<td>106.253</td>
</tr>
</tbody>
</table>

Table 19: $Y$ (given by equation 8.6) as a function of $1/T$ for Nb-1%Zr.
1 x 10^-10 J/m at all, and so Q_s and D_o can be deduced with reasonable certainty for the temperature range 900 to 1150°C. The least-squares slope yields Q_s as 178.89 kJ/mole, and the intercept (for a_s equal to 1 nm) provides D_o equal to 1.77 x 10^-5 m^2/sec.

The surface diffusion data of Allen (198) was derived from grain boundary grooving experiments performed on Nb containing 50 wt.ppm C, 40 wt.ppm O, and 10 wt.ppm N, at 1200°C and above. The equilibrium segregation of interstitials at such low concentrations and high temperatures will be negligible (see for example REF: 193), and so his D_o and Q_s values of 4.3 x 10^-5 m^2/sec and 194.2 kJ/mole, respectively, are representative of a 'clean' Nb surface. The D_o and Q_s values obtained from figure 43 - i.e. 1.77 x 10^-5 m^2/sec and 178.89 kJ/mole; respectively - are remarkably close to Allen's values which implies that Zr does indeed cleanse bubble surfaces of interstitials. It is unlikely that D_o and Q_s refer to Zr as the diffusing species because there will not be large quantities of Zr atoms present at bubble surfaces for 2 hour anneals below 1150°C. Furthermore, little is known about Zr diffusion on a Nb surface and so a quantitative assessment of D_o and Q_s in terms of Zr atom migration is not possible.

The ε value of 1 x 10^-10 J/m used above was obtained by applying equation (All.5) to the bubble size data at 950 and 1050°C with D_s given by Aitken's Nb results. If no assumptions are made regarding D_s, the ratio data in Table 17 of section 8.1 indicates that the lowest value of ε at these temperatures is ~ 5 x 10^-11 J/m. Using this lower value in equation 8.6, rather than 1 x 10^-10 J/m, modifies the data in Table 19 and figure 43 such that Q_s becomes 100.8 kJ/mole and D_o becomes 7.5 x 10^-13 m^2/sec, below 1150°C. D_o is particularly sensitive to the value of ε, whereas Q_s, although reduced, exhibits a minimum value which is comparable with the 105 kJ/mole found by Clum (200) for pure Nb from FEM measurements. Hence, both the minimum ε value of 5 x 10^-11 J/m and the 'most-likely' value of 1 x 10^-10 J/m reveal that Zr reduces the activation energy for Nb surface diffusion in a manner which can be explained if bubble surfaces are
In view of the surface cleansing role of Zr an analogous reduction in bubble size may also be expected if the 0 content of Nb is reduced. The variation of size in Nb containing 4, 68, 640, and 1538 wt.ppm 0, after 2 hours at 1050°C is summarized in Table 10 and figure 24 of Chapter 6. Bubble size does decrease as the 0 content is reduced but not as significantly as expected. Furthermore, a maximum size (and minimum number density) exists at 640 ppm 0, and bubbles in this and the 1538 ppm 0 sample were less distinctly faceted than in the other samples. Loomis et al. (210) have found that void swelling during high temperature, heavy-ion irradiation, is sensitive to the bulk 0 concentration which plays an important role in the nucleation process. Similar experiments performed with Nb coated with 0.3 μm Ti have revealed that substantial reductions in void volume-fraction are possible provided the bulk 0 concentration is lower than 500 at.ppm (211). This work demonstrates not only the gettering ability of Ti, but also that void nucleation and growth in Nb is dependent on the interstitial impurity level. However, the role played by interstitials is complex and is not yet fully quantified. Similarly, 0 no doubt influences the nucleation, and subsequent behaviour, of He bubbles in the Nb-0 alloys reported above, but the specific role of these impurity atoms cannot realistically be quantified from the small amount of data available. The results of section 6.3 in chapter 6 therefore only demonstrate that 0 does affect bubble size and density in Nb, while the reasons for some of the more specific observations must await a much more rigorous and systematic investigation.

8.3 RE-SATURATION AND BREAKAWAY IN Nb-0.3%Zr AND Nb-1%Zr

8.3.1 Bubble size re-saturation in Nb-0.3%Zr and Nb-1%Zr at 1050°C

A feature of the Nb-0.3%Zr and Nb-1%Zr ln(bubble size) vs. ln annealing time plots at 1050°C - which
are shown in figure 36 - is the sudden increase in bubble size between 15 and 30 hours which results in a new saturated size of 6.0 nm in both materials. When this phenomenon occurs there is also a reduction in bubble density which is clearly demonstrated by the Nb-1%Zr data given in Table 20, and plotted in figure 44. In this material densities of the order \( 4 \times 10^{22} \text{bubbles/m}^3 \) exist for times corresponding to the initial saturated size of 2.3 nm (i.e. up to 15 hours), but when the bubble size increases to 6.0 nm (beyond 30 hours) an order of magnitude reduction to \( \approx 3 \times 10^{21} \text{bubbles/m}^3 \) occurs. The presence of density reductions accompanying the size increase to 6.0 nm indicates that the re-saturation phenomenon occurs as a consequence of increased bubble mobility, and therefore an increased coalescence rate. It is possible to envisage that the sudden activation of vacancy sources could allow rapid bubble expansion as their excess pressures are equilibrated. Such a process is unlikely because a) there would be no significant change in bubble density, and b) the equilibration rate will be slow in terms of the anneals performed on these materials, even if the over-pressure approached the yield stress, and the vacancy concentration was many orders of magnitude greater than the thermal equilibrium level (see for example Chapter 7).

The breakaway/re-saturation phenomenon has no apparent effect on the total number of vacancies contained within bubbles. This is revealed by a simple, but crude, estimate based on the assumption that \( N_v \), the total number of vacancies in bubbles per unit volume, is given by the number of vacancies within the characteristic cube of dimension 'a' multiplied by the bubble density \( \rho \). i.e.

\[
N_v = \frac{a^3 \rho}{\Omega} \quad \text{...........}(8.7)
\]

where \( \Omega \) is the atomic volume which is given in Table 16. However, it was shown in chapter 6 that prolonged anneals at 1050°C produce some bubbles many times larger than the modal size. To account for these bubbles, which obviously contain most of the vacancies, \( M_v \) - the cube dimension based on the average bubble volume - is substituted for 'a' in equation 8.7. Thus if the various \( \rho \) values for
<table>
<thead>
<tr>
<th>Annealing Time (hours)</th>
<th>Bubble density $p \cdot \text{No.}/m^3$</th>
<th>Total No. of Vacancies in bubbles, $N_v/m^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$4.7 \times 10^{22}$</td>
<td>$1.7 \times 10^{26}$</td>
</tr>
<tr>
<td>4</td>
<td>$6.3 \times 10^{22}$</td>
<td>$3.5 \times 10^{26}$</td>
</tr>
<tr>
<td>15</td>
<td>$4.5 \times 10^{22}$</td>
<td>$3.6 \times 10^{26}$</td>
</tr>
<tr>
<td>40</td>
<td>$3.3 \times 10^{21}$</td>
<td>$3.1 \times 10^{26}$</td>
</tr>
<tr>
<td>70</td>
<td>$4.5 \times 10^{21}$</td>
<td>$2.2 \times 10^{26}$</td>
</tr>
<tr>
<td>100</td>
<td>$2.0 \times 10^{21}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 20: Bubble density in Nb-1%Zr as a function of time at 1050°C.

Figure 44: Bubble density as a function of annealing time for the Nb-1%Zr data in Table 20.
Nb-1%Zr given in Table 20 are used in conjunction with the relevant $M_V$ values in Table 13, $N_V$ is easily estimated from equation (8.7). The resultant $N_V$ data is summarized in Table 20. If bubbles equilibrated their excess pressures after every coalescence event during growth a gradual increase in $N_V$ might be expected with increasing annealing time. $N_V$ in Table 20 does not show this trend but tends to be approximately constant at $\sim 3 \times 10^{26}/m^3$. This provides a further indication of the excess pressures demonstrated in Chapter 7, particularly at prolonged annealing times which correspond to the change in saturated bubble size.

The application of equations (8.6) and (AII.5) in section 8.1 has shown that bubbles in Nb-0.3%Zr and Nb-1%Zr up to 15 hours grow by step nucleation limited migration and coalescence, with edge energies of $6.3 \times 10^{-11} J/m$ and $1.1 \times 10^{-10} J/m$, respectively. The application of equation (AII.5) to the 6.0 nm size plateau present beyond 30 hours in both materials, suggests that the same growth mode operates, but with the edge energy reduced to $\sim 4.3 \times 10^{-11} J/m$. This same 6.0 nm size plateau also exists in Nb-2.07%Zr after 8 hours at 1050°C. This implies that $\epsilon$ is again $\sim 4.3 \times 10^{-11} J/m$ but in this material there is no evidence of an initial smaller terminal size corresponding to a higher edge energy. To account for the reduction in $\epsilon$ in Nb-0.3%Zr and Nb-1%Zr it is necessary to invoke the segregation of a particular atomic species from the bulk to bubble surfaces. The long incubation period that exists before bubble size changes suggests that substitutional impurities, rather than interstitials, are involved. The existence of the same size plateau in all the Nb-Zr alloys, but in Nb-2.07%Zr after only 8 hours at temperature, implies that Zr is the most likely segregant.

It was shown briefly in section 8.2 that surfaces tend to be enriched with the alloy component having the lowest surface energy. Contributions to this enrichment are obtained if the solute atoms are bigger than the solvent atoms, and if the heat of solution is positive (188).
Miedema (188) and Tyson (189) have used extrapolation techniques to estimate $\gamma$ at $0^\circ$K for Nb and Zr, and they find 2570 to 2700 mJ/m$^2$ for Nb, and 1950 to 2070 mJ/m$^2$ for Zr. Experimental determinations of $\gamma$ have found 1850 mJ/m$^2$ for Zr at $1800^\circ$C, compared to 2100 mJ/m$^2$ for Nb at $2250^\circ$C (189). Zirconium has an atomic diameter of 0.319 nm compared to 0.294 nm for Nb (212), and so the size-mismatch strain energy in the matrix will be reduced if Zr is enriched at a surface. The heat of solution of Zr in Nb is unknown but calculations based on a sophisticated model for liquid metals provide a value of +17 kJ per mole of solute (213). It is clear, at least qualitatively, that Zr fulfills all of the conditions which normally indicate a preference for surface enrichment.

Equation 8.5, which is based only on surface energy, provided an enrichment factor $C^s_A/C^b_A$ of only 1.68 at $1050^\circ$C, although the exact value is to some extent dependent on the $\gamma$ values chosen for Nb and Zr. A similar factor due to size-mismatch alone can be estimated from the expression (188)

$$\frac{\ln C^s_A}{C^b_A} = \frac{0.42 KV \delta^2}{RT} \quad \ldots \ldots \ldots \ldots (8.8)$$

Here $V$ represents the molar volume, and $K$ the Bulk modulus. $KV$ is the average of the individual products for the solute $A$ and the solvent $B$, and $\delta$, the size mismatch parameter, is given by:

$$\delta = \frac{\langle V_A \rangle^{\frac{1}{3}} - \langle V_B \rangle^{\frac{1}{3}}}{\langle V_B \rangle^{\frac{1}{3}}}$$

where $\langle V \rangle^\frac{1}{3}$ is the average for the solute and solvent. Equation 8.8 assumes Poisson's ratio to be 0.3 for all materials, and that 25% of the mismatch energy remains when an atom reaches a surface, whereas more conventional expressions assume this energy to be zero at the surface (188). Using the tabulated data of Miedema (188) for Nb and Zr yields $KV = 15.5 \times 10^5$ kJ/mole, and $\delta = 0.084$, and so equation 8.8 provides $C^s_A/C^b_A = 1.52$ which is comparable to the 1.68 derived from the surface energy contribution alone (see section 8.2). This emphasizes the point that at normal equilibrium the first few atomic layers of a bubble surface
will be slightly enriched with Zr.

If the size-factor and surface energy contributions are additive then maximum surface concentrations of 0.96%, 3.2%, and 6.4% are to be expected for Nb containing 0.3%, 1%, and 2.07% Zr, respectively, at 1050°C. However, it was shown in chapter 7 that bubbles are over-pressurized, especially after long anneals, and so are biased sinks for vacancies. If there is any interaction between Zr atoms and vacancies a 'solute-drag' phenomenon - similar to that proposed by Antony (214) - could produce surface concentrations above the equilibrium level. Intuitively, some Zr-vacancy interaction is possible because the 'expansion' of an over-size solute atom into a nearest neighbour vacancy would reduce the size-mismatch strain energy. Michel and Moteff (215), studying voids in neutron irradiated and annealed Nb and Nb-1% Zr, have observed the suppression of void swelling in the alloy which they attribute to Zr-vacancy interactions. Furthermore, Smidt and Sprague (216) have proposed that void nucleation is suppressed by vacancy trapping at oversize solutes if their size is between 7 and 15% greater than that of the solvent atoms. The mismatch parameter for Zr in Nb falls within this range and so Zr-V interactions are feasible in the present work. However, it was shown in chapter 7, section 7.4, that the vacancy flux to bubbles is small compared to a dynamic irradiation situation, and so the extent of any non-equilibrium Zr enrichment at a bubble surface is unlikely to be very great.

The time needed to establish the equilibrium surface enrichments is dependent on the diffusivity of Zr in Nb at 1050°C, and may be estimated in the following manner. The bubble concentration in Nb-1% Zr after 1 hour is approximately $5 \times 10^{22}/m^3$ (see Table 20), and so assuming they are homogeneously distributed throughout the volume, each bubble can be considered as being positioned at the centre of a cube having a volume of $2 \times 10^{23} m^3$. For bubbles having cube dimensions of 2.3 nm the inter-cavity spacing is 24.8 nm, and the time taken for a Zr atom to diffuse half this distance, $x$, to one bubble is given by the one-dimensional diffusion

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equation as:
\[ t = \frac{x^2}{2D_{Zr}} \] ...................(8.9)

The diffusion coefficient of Zr in Nb at 1050°C has not been ascertained reliably, but Einziger and Mundy (217) have measured the diffusivity of Zr between 1650 and 2250°C and find \( D_0 = 8.5 \times 10^{-3} \text{ m}^2/\text{sec} \), and \( Q_{Zr} = 3.93 \text{ eV} \). Extrapolating from their data to 1050°C provides \( D_{Zr} = 5.56 \times 10^{-20} \text{ m}^2/\text{sec} \).

Prokoshkin and Vasileva (155) have presented graphically some early Russian Zr tracer results on the dependence of \( D_{Zr} \) with composition at 1000, 1200, and 1600°C. Using their value for Nb-1%Zr - i.e. \( D_{Zr} \sim 10^{-20} \text{ m}^2/\text{sec} \) - at 1000°C, and \( x = 12.4 \text{ nm} \), equation 8.9 provides \( t = 2.05 \text{ hours} \).

Clearly, the equilibrium surface concentration is achieved at an early stage during annealing, and so bubble surfaces at times corresponding to the first size plateau in Nb-0.3%Zr and Nb-1%Zr will have different Zr enrichments. As the bulk Zr concentration increases the Zr content of a bubble surface increases, and the surface energy is marginally decreased. Consequently \( \varepsilon \) will be reduced but not significantly as the surface energies of Nb and Zr are very close. This reduction with increasing Zr enrichment will be more than offset by the increase in \( \varepsilon \) resulting from the gettering of interstitial impurities (see section 8.2). Zirconium segregation alone, therefore, cannot explain a) the reduction of \( \varepsilon \) from 6.3 \times 10^{-11} \text{ J/m} \) and 1.1 \times 10^{-10} \text{ J/m} in Nb containing 0.3% and 1% Zr, respectively, to 4.3 \times 10^{-11} \text{ J/m} between 15 and 30 hours, or b) why this same edge energy exists in Nb-2.07%Zr as well.

It was proposed in section 8.2 that bubble surfaces are initially cleansed of interstitials due to trapping at Zr atoms in the matrix. The internal friction results of Dunn et al. (203) suggest that the Zr - O binding energy is high, and so 0 in particular, and interstitials in general, may retard the Zr diffusivity. If \( D_{Zr} \) for those Zr atoms interacting with 0 is reduced by a factor between 2 and 10 - i.e. Prokoshkin and Vasileva's value of 10^{-20} \text{ m}^2/\text{sec} (155) becomes 5 \times 10^{-21} \text{ and } 10^{-21} \text{ m}^2/\text{sec} \), respectively - then equation 8.9 provides a segregation time of between 4.2 and 21.4 hours for \( x = 12.4 \text{ nm} \).
This broadly encompasses the 15 hour incubation period for the £ reduction in Nb-0.7%Zr and Nb-1%Zr, and so suggests that the arrival of Zr-0 defects at the bubble surface could be significant.

An interesting feature of dilute Nb-Zr alloys containing 0 is their ability to age-harden during prolonged annealing. If the 0 content exceeds the solubility limit alloys can be aged to produce precipitates of monoclinic ZrO\textsubscript{2}, or a coherent metastable transition phase (like ZrO) which terminates in ZrO\textsubscript{2} (218). Thurber et al. (219) have demonstrated this with Nb-1%Zr containing 3100 wt.ppm 0, but the phenomenon also occurs with much lower 0 concentrations (218). The solubility limit of 0 in Nb-0.88%Zr at 1600\(\degree\)C is 300 wt.ppm (218), while Bryant (156) has considered the limit to be lower than 0.5 at.% (860 wt.ppm) at 1050\(\degree\)C. The actual 0 content of the Nb-0.3%Zr and Nb-1%Zr investigated here is unknown, but it is likely to be of the same order as that in the Nb-2.07%Zr - i.e. \(\sim\)615 wt.ppm. Although this is close to the solubility limit no precipitation was observed in any of these alloys at this temperature, and so the Zr-0 in the bulk probably exists as a mixture of mono-interstitial and di-interstitial defects, as proposed by Miner et al. (205).

The driving force for the segregation of Zr-0 defects to bubble surfaces will arise from the surface energy reduction on their arrival. The surface energy of ZrO\textsubscript{2} is 590 mJ/m\(^2\) (220) compared to 2100 mJ/m\(^2\) and 1850 mJ/m\(^2\) for Nb and Zr (189), respectively, and so it is reasonable to expect that the arrival of Zr-0 defects at a bubble surface will produce a more dramatic reduction in \(\gamma\),and \(\varepsilon\), compared with that of Zr alone, even though ZrO\textsubscript{2} itself is unlikely to be formed. The total number of Zr-0 defects in the bulk is limited by the 0 content of the alloy, rather than the Zr concentration. If the 0 content of each alloy is 615 wt.ppm (\(\sim\)0.36 at.\%) then to a first approximation the concentration of Zr-0 defects will be the same in each material. (This is reasonable for Nb-1%Zr and Nb-2.07%Zr because the ratio of the number of Zr to 0 atoms is \(\sim\)3:1 and \(\sim\)6:1, respectively.)
However, this may not be strictly true for Nb-0.3\%Zr where the ratio is only 1:1. Consequently, the equilibrium surface concentration of Zr-O defects should be similar in all the alloys, and the edge energy will be constant. Thus, on the basis of the qualitative arguments employed above, the presence of Zr-O defects, and more particularly their segregation to bubble surfaces, can provide an explanation for the breakaway-resaturation phenomenon in Nb containing 0.3 and 1\% Zr, and the results for Nb-2.07\%Zr at the same temperature.

The effect that a reduction in $\epsilon$ has on bubble mobility, and therefore the growth rate, can be gauged more quantitatively with reference to Figure 45. The bubble diffusion coefficient, $D_b$, based on surface diffusion and step nucleation control are given by equations AI.2 and AI.3 in Appendices I and II, respectively. Figure 45 shows how $D_b$ varies with the controlling kinetics, bubble size, and edge energy, at 1050°C assuming that $D_s = 5.8 \times 10^{-13} \text{ m}^2/\text{sec}$, the value which matches Aitken's data for Nb at this temperature - $a_s = 1.0 \text{ nm}$, and $\Omega = 1.79 \times 10^{-29} \text{ m}^3$. If step nucleation is the limiting process then Figure 45 clearly demonstrates that any change to the edge energy, $\epsilon$, has a dramatic effect on the bubble mobility. For example, a 2.5 nm bubble and an edge energy of $1 \times 10^{-10} \text{ J/m}$ which corresponds to the Nb-1\%Zr data up to 15 hours, has a $D_b$ of $2 \times 10^{-22} \text{ m}^2/\text{sec}$. This is almost 5 orders of magnitude slower than if the bubble was limited by surface diffusion, but a reduction in $\epsilon$ from $1 \times 10^{-10} \text{ J/m}$ to $8 \times 10^{-11} \text{ J/m}$ increases $D_b$ by two orders of magnitude to $2 \times 10^{-20} \text{ m}^2/\text{sec}$ if the bubble size does not change. A very dynamic situation exists when segregants arrive at bubble surfaces in sufficient quantities to reduce $\epsilon$.

For example, the edge energy in Nb-1\%Zr will reduce gradually from $1 \times 10^{-10} \text{ J/m}$ with the arrival of segregants from the bulk, until the equilibrium surface composition is achieved and $\epsilon$ stabilizes at $4.3 \times 10^{-11} \text{ J/m}$. Any increase in bubble mobility due to a small reduction in $\epsilon$ will be compensated by an increase in bubble size which arises from an enhanced collision frequency. Consequently when $\epsilon$ stabilizes at $4.3 \times 10^{-11} \text{ J/m}$ the actual mobility of a 6.0 nm bubble is much

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Figure 45: The bubble mobility for surface diffusion and ledge nucleation limited migration, as a function of size and edge energy.

(The broken lines represent ledge nucleation limited migration for the particular $\varepsilon$ value indicated, whereas the solid line DC corresponds to surface diffusion control.)
the same as that for a 2.5 nm bubble with $\varepsilon = 1 \times 10^{-10} \text{J/m}$.

Figure 45 also indicates that the actual kinetic mechanism limiting the mobility of cubic bubbles in Nb is dependent on the edge energy, and, therefore, the composition and cleanliness of the bubble surface. If, for example, $\varepsilon = 3 \times 10^{-11} \text{J/m}$ then bubbles will be surface diffusion limited until their average size corresponds to that at point A in the figure, because $D_b$ for step nucleation control lies to the left of the surface diffusion line BC. When the characteristic size exceeds that specified by point A the controlling kinetics will change to a step nucleation mechanism, and there will be a characteristic change of slope on a log(size) vs. log(annealing time) plot as, for example, exhibited by Aitken's Nb data (see section 8.1). Clearly, if solute additions increase $\varepsilon$ to $6 \times 10^{-11} \text{J/m}$ or greater, then bubble mobility will be step nucleation limited for all sizes observable in the TEM. The position of all the curves in figure 45, with respect to each other, is unchanged if different $\alpha_s$ and $\gamma$ values are used, although the $D_b$ axis must be adjusted accordingly. The edge energy, and its variation with a small substitutional solute addition, therefore has a marked effect on the controlling kinetics in Nb. Furthermore, the breakaway/re-saturation phenomenon in Nb-0.3%Zr and Nb-1%Zr can be explained without invoking a change in the bubble growth mechanism, if $\varepsilon$ is reduced by a segregation process which involves solute interstitial clusters.

8.3.2 Bubble size breakaway in Nb-1%Zr at 1250°C

Helium bubbles in Nb-1%Zr at 1250°C are always faceted and have the same general $\{100\}$ and $\{100\}/\{110\}$ morphologies described in chapter 6. Anneals of 1 hour or shorter produce a constant bubble size of 4.8 nm that is consistent with a step nucleation limited, migration and coalescence growth mode with $\varepsilon = 6 \times 10^{-11} \text{J/m}$. This edge energy is lower than the $1 \times 10^{-10} \text{J/m}$ deduced for 950 and 1250°C, but is still greater than the $1.4 \times 10^{-11} \text{J/m}$ obtained from

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Aitken's Nb results at this temperature (see Table 17).

The edge energy for Nb containing 400 wt. ppm O at 1050 and 1250°C shows little variation with temperature (see Table 17), and in view of the constant value of $1 \times 10^{-10}$ J/m for Nb-1% Zr at 950 and 1050°C it may seem surprising that $\xi$ at 1250°C is only $6 \times 10^{-11}$ J/m. However, as the temperature rises the surface energy and size mismatch enrichment factors, given by equations 8.5 and 8.8, respectively, are both reduced. For example, the surface energy contribution given by equation 8.5 provides $C_{\text{Zr}}^S/C_{\text{Zr}}^b = 1.57$ at 1250°C compared with 1.68 at 1050°C, and so the equilibrium Zr concentration at a bubble surface reduces at higher temperatures. If the Zr-O complexes, which were proposed to explain the cleansing of bubble surfaces in section 8.2, are stable at 1250°C then their equilibrium surface concentration will be reduced in a similar manner. Consequently, any breakaway/re-saturation phenomenon at this temperature which involves these defects will provide $\xi$ slightly greater than the $4.3 \times 10^{-11}$ J/m found at 1050°C (i.e., less complexes are available to contribute to the reduction from $1 \times 10^{-10}$ J/m).

The segregation time for Zr-O complexes at 1250°C can only be estimated on the basis of $D_{\text{Zr}}$ which is effectively unknown for this temperature. Extrapolating from the tracer results of Einziger and Mundy (217) provides $D_{\text{Zr}} = 5.48 \times 10^{-18}$ m$^2$/sec, whereas Prokoshkin and Vasileva (155) give approximately $4 \times 10^{-19}$ m$^2$/sec at 1200°C. If $D_{\text{Zr-O}}$ at 1250°C is $4 \times 10^{-19}$ m$^2$/sec (i.e., equivalent to $D_{\text{Zr}}$ at 1200°C) then a complex can diffuse 20 nm in one direction within 8 minutes. This implies that the equilibrium Zr-O surface concentration always exists and so the small step nucleation limited portion at this temperature probably corresponds to the breakaway/re-saturation region at 1050°C. There is no breakaway portion to the 950°C results (see Figure 40a), but it does occur between 15 and 30 hours at 1050°C and so it is not unreasonable to expect it to occur at shorter times for higher temperatures. Further evidence for this conclusion is provided by the fact that $\xi = 6 \times 10^{-11}$ J/m, compared to $4.3 \times 10^{-11}$ J/m.
at 1050°C, in keeping with the effect of the enrichment factor reduction noted above.

For anneals longer than 1 hour the modal bubble size dramatically increases to 85 nm - which is well beyond the 25 nm corresponding to the 1250°C size plateau in Aileen's Nb - within 40 hours. This size increase is not linear with annealing time in figure 40c and so it is not possible to use a slope to determine whether the bubble growth mechanism, or controlling kinetics, has changed. However, at this temperature (but not at lower temperatures) the fringed images shown in figure 46 were observed in the matrix of samples corresponding to the breakaway portion of the growth curve. In bright-field - figures 46 a) and c) - the contrast exhibited by the outer fringes is different, whereas in dark-field - figures 46b) and d) - it is the same. These features are characteristic of δ- boundaries which often arise as a result of an ordering process that differently distorts two parts of a crystal (221,222). The fringes run parallel to the foil surface and mark the boundary of two domains which have slightly different s or g values for the same operating reflection.

Gevers et al. (222), and Van Landuyt et al. (223), have previously observed these coherent domain boundaries in Nb that had been annealed at 1500°C for 2 hours in a vacuum of 10⁻⁵ Torr. Low intensity superlattice reflections were observed in diffraction patterns and they deduced that domains formed as a result of the ordering of 0 interstitials in a manner that produced a slight deformation of the Nb lattice in ⟨110⟩ directions. Boundaries were not strictly defined by specific crystallographic planes, but there was a tendency to be parallel to {100} and {211} planes (223). The boundaries observed in the present work exhibited a similar tendency but no regular supplementary spots were observed in diffraction patterns from these regions. Consequently, a more quantitative assessment of the ordering process is not possible but 0 is the most likely interstitial producing the phenomenon, although domain boundaries displaying δ- fringes have also been observed in ordered Nb β-hydride (224).
Figure 46: $\delta$-fringes in Nb-1\%Zr after 8 hours at 1250°C

- a) & c) Bright-field (different areas) with $g_{101}$.
- b) Dark-field to a) using a $10\bar{1}$ reflection.
- d) Dark-field to c) using a $\bar{1}0\bar{1}$ reflection.

0.2 $\mu$m
Apart from this ordering phenomenon bubbles on the breakaway portion of the 1250°C growth curve have distinct strain fields - as shown in figure 47 . Ashby and Brown (167) have shown that the strain contrast image width of a spherical inclusion of radius \( r_o \) is determined by the parameter:

\[
\frac{\lambda r_o^3 \xi}{\xi^2}
\]

Here \( \lambda \) is the misfit parameter that specifies the sign and magnitude of the displacements, \( \xi \) is the reciprocal lattice vector of the operating reflection, and \( \xi \) is the extinction distance. For non-spherical shapes \( r_o \) is replaced by \((3V/4)^{\frac{1}{3}}\) where \( V \) is the bubble volume (167). It is possible, therefore, to estimate \( \lambda \) by measuring image widths as a function of bubble size for known diffraction conditions. (Okamoto et al. (225) used this method to analyse segregation induced strain fields around voids in Vanadium). Such measurements were performed on 30 cubic - not truncated - bubbles in Nb-1%Zr after 8 hours at 1250°C, with \( g = 200 \). The cube dimensions of these bubbles were between 9 and 15 nm, and \( \lambda \) was found to be variable within the range \( 0.5 \times 10^{-3} \) to \( 1.15 \times 10^{-2} \).

Brown and Mazey (226) have given the misfit parameter of a gas-containing cavity as:

\[
\lambda = \frac{1}{hG} \Delta P_{\text{ex}}
\]

where \( \Delta P_{\text{ex}} = (P - 2Y/r) \)

\( h \) is the excess pressure, and \( G \) is the shear modulus which is approximately \( 37.5 \times 10^3 \) MN/m\(^2\) for Nb (184) at 20°C. If the strain fields were caused by excess pressure alone then \( \Delta P_{\text{ex}} \) would need to be \( \approx 675 \) MN/m\(^2\) for \( \lambda = 4.5 \times 10^{-3} \). This exceeds the Nb yield stress of \( 170 \) MN/m\(^2\) at 20°C (184) and so bubbles might be expected to show signs of dislocation generation. No evidence for this was observed, so the strain fields probably arise from the co-operative effects of an over-pressure and a change in structure and composition of the bubble surface due to the ordering process. This latter possibility is not
FIGURE 47 (a): Strain fields around bubbles in Nb-1%Zr after 8 hours at 1250°C.

An example of the 20% strain field image width (as defined by Ashby and Brown (167)) assumed during measurement is shown in the micrograph. The extinction distance, $\xi$, for a Nb 200 reflection was taken as 36.7 nm (see Appendix to Ref. 221).
Figure 47 (b): Strain fields around bubbles in Nb-1%Zr after 8 hours at 1250°C.

Figure 47 (c): Unusual strain fields around bubbles in Nb-1%Zr after 25 hours at 1250°C.
unreasonable because the Zr concentration at the bubble surface will be slightly higher than in the bulk, and so it may be possible to form localized areas of a Nb-Zr-O sub-oxide which contains more Zr than in the bulk. Zirconium atoms are over-sized in Nb and so the presence of such a phase at the surface will produce strain fields. Some indication that a second phase is present at bubble surfaces is provided by the fact that localized, irregular strain fields - as shown in Figure 47(c) - are often observed around some bubbles.

If the surface does incorporate areas of a sub-oxide phase then the bubble mobility can be dramatically increased without a change in the controlling kinetics or the growth mode. The surface energies of oxides are generally lower than those of pure metals (see, for example, REF: 220), and so for a surface containing an ordered sub-oxide can be much lower, dependent on the actual composition, than the value deduced for Nb contaminated with essentially adsorbed O. Consequently, bubble size will be increased in a manner analogous to that described in section 8.3.1, until the size population becomes characteristic of the new value. There is no re-saturation of bubble size in figure 40c, and so equation 8.2 with and indicates that must be smaller than for this mechanism to be feasible. It appears, therefore, that the breakaway phenomenon in Nb-1%Zr at 1250°C could be caused by a reduction in due to the ordering process, rather than a change in the actual growth mode or limiting kinetics.

8.4 THE DEVELOPMENT OF LARGE BUBBLES

It was shown in chapter 6 that He bubbles in Nb-1%Zr and Nb-2.07%Zr (and also to some extent in Nb-0.3%Zr) at 1050°C have non-uniform size distributions. As the annealing time increases the size histograms - for example those in figures 30 and 34 - develop distinct tails which extend to larger sizes. This gradual development of relatively few extremely large bubbles is clearly demonstrated by the
micrographs in figure 20. Potentially there are a number of mechanisms by which these large bubbles could be produced. Stress and temperature gradients are known to bias bubble migration, and intrinsic microstructural effects such as the channelling of bubbles by dislocations, or grain boundary sweeping, could also be responsible for the phenomenon. Stress gradients are not likely to be responsible for such large bubbles because the implanted samples were free from applied macroscopic stresses during annealing. Furthermore, Martin (24) has shown that although stress gradients do influence the direction of bubble migration, the enhanced coalescence resulting from the effect at 1000°C is insignificant in comparison with the effect of a temperature gradient.

The force on an atom due to a temperature gradient $dT/dx$ in one dimension, is (85, 86):

$$F = -\frac{Q_i^*}{T} \frac{dT}{dx}$$

The parameter $Q_i^*$ denotes the heat of transport of a diffusing atom and it will differ for diffusion through a vapour, through the lattice, or along a surface. In simple terms it can be considered as the heat carried by a single atom as it moves down the gradient (85). Consider a [100] cubic bubble of dimension 'a' that moves a distance $dx$ in a [100], up the gradient $dT/dx$. A total of $(a^2 dx)/\Omega$ atoms must be transferred down the gradient from one cube face to the opposite face - i.e. through a distance a - and so the net force exerted on the bubble by the gradient is:

$$F_b \sim \frac{a^3}{\Omega} F$$

or

$$F_b \sim -\frac{a^3 Q_i^*}{\Omega} \frac{dT}{T} dx \quad \ldots \ldots (8.10)$$

Barnes and Nelson (73) have proposed that $F_b$ must be $10^{-12} N$ or greater to have a significant influence on migration and coalescence. Thus, using this value for $F_b$, and
typical values for the other parameters, the minimum
temperature gradient that will bias bubble migration can be
estimated from equation 8.10.

Shevmon (183) has shown that $Q^*$ is equal to, or less than, the activation energy for an atomic jump of the
diffusing species. Since atoms are transferred around the inside
surface of the bubble, $Q^*$ has a magnitude approximately the
same as the activation energy per atom for surface diffusion.
In section 8.2 it was shown that in Nb-1%Zr between 900 and
1150°C $Q_s$ is approximately 178.89 kJ/mole $(2.97 \times 10^{19} \text{J per}
atom)$, and so at 1050°C, with $a = 2.5 \text{nm}$ and $\Omega = 1.79 \times 10^{-29} \text{m}^3$,
equation 8.10 provides $dT/dx = 5.1 \times 10^6 \text{K/m}$. Similarly, if
$Q_s$ corresponds to 332.8 kJ/mole $(5.52 \times 10^{19} \text{J/atom})$ - which is
the value deduced from Aitken's results for Nb at this
temperature - then $dT/dx$ must still be greater than
$2.7 \times 10^6 \text{K/m}$ for significant biasing. These gradients imply
that the temperature differential across the foil thickness
during annealing must be $270 - 510 \text{K}$ or greater. Such
differentials do not exist and so thermal gradients cannot be
responsible for the development of very large bubbles.

A more feasible mechanism, particularly for
high bubble densities, would be the channelling of smaller
bubbles attached to dislocation, to dislocation nodes. Bubbles
experience an attractive force from dislocations (136), and
when attached to a dislocation a bubble is clearly at a
position of minimum energy because a length of imperfection
equivalent to a bubble diameter must be created if it were
removed. If there is no driving force tending to detach the
bubble, or if the driving force for dislocation motion is low,
then the cavity can only move along the imperfection line. The
pair-wise coalescence time of surface-diffusion limited
spherical bubbles has been analysed by Speight (139), but
bubbles in Nb-Zr alloys are faceted and limited by ledge
nucleation. Beere (118) has shown that the intersection of
a bubble facet by a screw dislocation reduces the critical
ledge nucleation energy $\Delta G^*$. Consequently the ledge nucleation
frequency - given by equation 7.7 - is increased and the
bubble mobility along the imperfection line is greater than for unattached bubbles limited by the same kinetics. The behaviour of bubbles intersected by dislocations apart from pure screws will be more complex, but again the mobility is likely to be enhanced (118).

However, Shiraishi et al. (116) have studied Helium bubble growth in both annealed and 8% cold worked Aluminium during isothermal anneals of up to 100 hours, and found that the cold-work did not cause any extra coarsening of the bubble population. In the present study of Nb-Zr alloys, neither all the small bubbles, nor all the larger ones, were observed to be on dislocations, and so it seems unlikely that bubble migration along dislocations is responsible for the development of very large bubbles in these materials. Another microstructural feature that could produce large matrix bubbles is grain boundary sweeping. For this process to be important the driving force for boundary motion \( F_{gb} \), must be equal to the pinning force, \( F_p \), exerted by the bubble (114). In this situation a high concentration of bubbles is produced within the boundary as it moves, and the resultant enhanced coalescence leads to detachment from the boundary when they have grown to a critical size (140). This phenomenon has been reported in Aluminium during post-implantation annealing above 0.9\( T_m \) (116).

If, however, \( F_{gb} > F_p \) then there is no interaction between bubbles and a mobile boundary (see, for example, references 115 and 142), and for \( F_p < F_{gb} \) the boundary will be effectively pinned. The Nb-Zr alloys investigated here were fully recrystallized before implantation and so \( F_{gb} \) is expected to be small during subsequent anneals at approximately 0.5 \( T_m \). Bubbles on boundaries were faceted and larger than their matrix counterparts, but no adjacent bubble-free zones indicative of sweeping were apparent. These points are illustrated in figure 48. Furthermore, the large bubbles in these alloys appear to be randomly distributed throughout the matrix — see, for example, figure 20(c) — whereas a bubble sweeping mechanism would tend to localize them near the boundary, especially if the boundary mobility is low. There is
Figure 48: Grain-boundary bubbles in Nb-1%Zr after 1 hour at 1050°C.

a) Bubbles on an inclined boundary which are much larger than the matrix ones.

b) The absence of bubble free zones adjacent to the boundary.
no evidence, therefore, to support a grain boundary sweeping mechanism, and so large bubbles must be generated by more subtle processes than those considered up to now.

Lidiard and Nelson (227) have shown that weak strain fields should exist around bubbles even when they are at thermodynamic equilibrium, because of the inherent difference between surface energy and surface tension. Consequently, there is always a finite interaction energy, \( E \), between two bubbles because each perturbs the stress field of the other. The concepts involved in the calculation of \( E \) have been developed by Eshelby (228), who has considered the analogous problem of the interaction between two spherical inclusions. If the inclusions are considered to have been inserted into holes which are slightly too small for them their interaction energy, \( E \), is the sum of the resultant misfit energy, \( E_{\text{mis}} \), and an energy term, \( E_{\text{inh}} \), that accounts for the defect's role as an elastic inhomogeneity (229). i.e:

\[
E = E_{\text{mis}} + E_{\text{inh}} \quad \ldots (8.11)
\]

\( E_{\text{mis}} \) is related to the dilation induced by the small cavity when the inclusion is inserted, but if the inclusion produces only radial lattice displacements, and the material is isotropic, it can be shown that \( E_{\text{mis}} = 0 \) (229). Consequently, \( E = E_{\text{inh}} \), where

\[
E_{\text{inh}} = aK W_d + \frac{aG W_s}{G} \quad \ldots (8.12)
\]

\( W_d \) and \( W_s \) are the dilational and shear parts of the energy density, respectively, whereas \( K \) and \( G \) are the constants given by Dewey (230) for a dilute suspension of spheres of bulk modulus \( K' \) and shear modulus \( G' \) in a solid having moduli \( K \) and \( G \). Thus, for a spherically symmetric displacement field, and an isotropic solid, \( W_d = 0 \) and (229):

\[
E = aK W_s
\]

The variation of \( E \) with the inclusion spacing \( l \) is obtained
by substituting for $a_G$ (230), and $W_n$ (228, 229). If gas bubbles are considered as spherical inclusions which have zero shear modulus, then the interaction energy of two bubbles a and b, a distance $l$ apart, is (227):

$$E = \left( a^a v_b + a^b v_a \right) \frac{p}{l} \ldots \ldots (8.13)$$

where

$$\beta = -6G \left\{ 1 - \frac{2(\mu - 5\nu)}{15(1 - \nu)} \right\}^{-1}$$

Here $V$ indicates the volume of the respective bubble, and $c$ is the bubble 'strength' which can be found from a balance of the forces on the internal, and an external surface. The $l^{-6}$ dependence is the same as that for the interaction of solid inclusions (228, 229).

Willis and Bullough (231) have more rigorously investigated bubble interactions, and have derived an analytical solution for $E$. However, they note that for $V = \frac{1}{3}$ equation 8.13 can be expressed in terms of the bubble radii $r$ and $r_1$, and their respective pressures $P$ and $P_1$, as:

$$E = -\frac{15\pi r^3 r_1^3}{16 G l^6} \cdot \left\{ \left( \frac{P - \frac{2\gamma}{r}}{r} \right)^2 r^3 + \left( \frac{P_1 - \frac{2\gamma}{r_1}}{r_1} \right)^2 r_1^3 \right\}$$

$$\ldots \ldots (8.14)$$

where $G$ is the shear modulus.

Since $F = -\frac{de}{dl}$, bubbles experience an attractive force which is proportional to $l^{-7}$ whenever an excess pressure exists. (The distinction between surface energy and surface tension means that bubbles at thermodynamic equilibrium will also be very slightly over-pressurized (231)). The force $F$ clearly reduces rapidly with increasing bubble separation and so it can only influence coalescence over a short range (227,231). If, for example, two bubbles having radii 1.5 and 5 mm contain arbitrary over-pressures of 5 and 50 MN/m$^2$, respectively, then differentiating equation 8.14 (with $G$ for Nb equal to $37.5 \times 10^9$ N/m$^2$ (184)) reveals that $F > 10^{-12}$N for $l < 5$ mm. Barnes and Nelson (73) have considered that $F$ must exceed

- 170 -
10^{-12} \text{N} to significantly bias bubble migration, and so clearly there is no long range interaction that could account for the presence of large bubbles.

However, this conclusion relies heavily on two assumptions, namely a) that the bubble has spherical symmetry so that it creates only a radial displacement field, and b) that the solid is completely isotropic. Bubbles in Nb-Zr alloys have a cubic morphology, and most materials - including Nb - have anisotropic elastic properties. If a point defect, or an inclusion, is not quite spherical but can be described by a cluster of six equal forces which act radially outwards at the face-centres of a cube having dimension a, then even in an isotropic solid a dilation term exists which makes $E_{\text{mis}}$ in equation 8.11 non-zero (229). Eshelby (229) gives

$$E_{\text{mis}} \propto \frac{a^2 \Gamma}{l^5}$$

where $\Gamma$ is an angular factor which is dependent on the position of the two bubbles with respect to each other. This $E_{\text{mis}}$ term dominates the total interaction energy because it is slightly longer ranging, and so by analogy, it is possible that non-spherical bubbles in isotropic solids do experience a longer ranging (but highly directional) attractive force than implied by equations 8.13 and 8.14.

The interaction energy $E$ between a pair of defects, or inclusions, in a cubic, anisotropic crystal, has been given approximately by Eshelby (228, 229, 232) as:

$$E = -\frac{15}{8\pi w^2} \frac{\Delta V_1 \Delta V_2 d \Gamma}{l^3} \ldots \ldots (8.15)$$

Here $w = (3(1 - v)/(1 + v))$ where $v$ is Poisson's ratio, $\Delta V$ is the volume change produced by the defect, $d = c_{11} - c_{12} - 2c_{11}^2$, where $c_{11}$, $c_{12}$, and $c_{11}^2$, are the relevant elastic constants, and $\Gamma$ is the angular factor which has a minimum of $-0.27$ in $\langle 111 \rangle$, a maximum of $+0.4$ in $\langle 100 \rangle$, and a value of $-0.1$ in $\langle 110 \rangle$ directions (232). Thus, dependent on the sign of $d$, and
the $\Delta V$ terms, there are always certain directions where a long range attractive force, which is proportional to $1^{-4}$, exists. Willis (233) has more rigorously analysed the interaction between two spherical bubbles of equal size in an anisotropic solid, and has come to the same conclusion. He presented the interaction energy in the form

$$E = \left( \frac{P - 2\gamma}{r} \right) r^3 \left\{ E_0 \left( \frac{r}{1} \right)^3 + E_1 \left( \frac{r}{1} \right)^5 + E_2 \left( \frac{r}{1} \right)^6 \right\}$$

where the coefficients $E_0$, $E_1$, and $E_2$, are dependent on $d$, $G$, and $\Gamma$. Willis (233) has applied this equation to bubbles in $\alpha$-Uranium to verify that there are particular crystallographic directions where a significant long-range bubble interaction energy exists.

It is feasible, therefore, that such long range bubble interactions could be responsible for the growth of the large bubbles observed in the Nb-Zr alloys. If the attractive force between a large bubble and a smaller one is greater than that between two small ones, a net drift of small bubbles to larger ones can be envisaged. This drift would be more pronounced in some directions, but the overall effect would be to enlarge the big bubbles without producing bubble-free zones around them. The development of large bubbles would occur gradually with increasing time at temperature - as in fact observed, for example, in Nb-1\%Zr at 1050°C (figure 30) - because bubble migration is essentially slow. Unfortunately, the nature of the displacement field produced by {100} cubic, or brick-shaped, bubbles containing excess pressures, is uncertain and so it is not possible to further quantify the feasibility of long range bubble interactions in these alloys. However, since significant long range interactions exist between two spherical bubbles of equal size in $\alpha$-Uranium, it is certainly possible that such interactions could contribute to the features of the size-distributions observed in Nb-Zr alloys - particularly as the bubble density is high.

Apart from bubble - bubble interactions
larger bubbles may be developed by an alternative mechanism which involves a change in edge energy due to segregation of solute-interstitial defects. It was proposed in section 8.3.1 that the segregation of such defects - particularly Zr-0 - is responsible not only for the breakaway/re-saturation phenomenon in Nb containing 0.3% and 1% Zr at 1050°C, but also for the existence of the same size plateau in Nb-2.07%Zr. Although the net effects of segregation at 1050°C do not manifest themselves in the vast majority of bubbles until approximately 15 hours, significant quantities of segregant will reach some bubbles in the population much earlier - especially if the Zr-0 defect distribution is not perfectly homogeneous. Consequently, some bubbles may have a lower edge energy (and consequently a higher mobility \(D_b\) (equation AII.3)), but the same size as the majority in the population.

Consider, for example, a population of 2.5 nm bubbles in a material with \(\varepsilon = 1 \times 10^{-10} \text{J/m} \). This is typical of Nb-1%Zr after approximately 1 hour at 1050°C. Figure 45 provides a \(D_b\) of \(2 \times 10^{-22} \text{m}^2/\text{sec}\) for these conditions, but if segregation has reduced the edge energy of say 10% of these bubbles to \(8 \times 10^{-11} \text{J/m}\) then their mobility is two orders of magnitude greater at approximately \(2 \times 10^{-20} \text{m}^2/\text{sec}\).

It can be shown from equation AII.3 that the coalescence rate is increased and so the 10% of bubbles which have \(\varepsilon = 8 \times 10^{-11} \text{J/m}\) will undergo accelerated growth. However as they grow their mobility is reduced until at 3.5 nm it is comparable to that of a 2.5 nm bubble with \(\varepsilon = 1 \times 10^{-10} \text{J/m}\) - see figure 45. Thus the large bubbles are not necessarily immobile. If the edge energy of these bubbles is lower than \(8 \times 10^{-11} \text{J/m}\), then potentially even larger bubbles may be developed. Once a small population of large bubbles exists there are a number of factors that could ensure its growth with increasing time at temperature. There will be normal random collisions between small and large bubbles, and there is also a small, but finite, probability that large bubbles will collide with other large bubbles. The frequency of such events is described by equation (AII.3), which is based on the
theory of colloid coagulation developed by Chandrasekhar (89), but these collision frequencies may be significantly enhanced if there are long-range interaction effects as described previously. Furthermore, these larger bubbles will contain a higher relative excess pressure than smaller ones, and so they are potentially more susceptible to non-equilibrium (i.e., vacancy drag induced) segregation effects which may lower their edge energy even more.

Some qualitative evidence that the production of large bubbles in Nb-Zr alloys is related in some way to the presence of Zr, is supplied by the size histograms shown in figures 25, 30, and 34. The development of the size histogram tail in Nb-0.3%Zr (figure 25) at 1050°C is not pronounced, whereas it can be clearly followed in Nb-1%Zr and Nb-2.07%Zr (figures 30 and 34, respectively). Furthermore, an analysis of size distributions in Nb at this temperature does not reveal any of these features. In summary, therefore, the presence of bubbles which have many times the modal size cannot be explained by grain boundary sweeping, dislocation channelling, or stress and temperature gradients. It is possible that long range bubble interactions are responsible for the development of large bubbles, but it seems more likely that a reduction of the edge energy of some bubbles due to solute-interstitial complex segregation after only short anneals, is more important - at least initially. However, this change in ε and bubble-bubble interactions may be co-operative features in the subsequent growth of these bubbles.

8.5 SUMMARY

Helium bubbles in Nb grow by migration and coalescence during post-implantation annealing at 950, 1050, and 1250°C. Bubble mobility is limited by surface diffusion throughout 100 hour anneals at 950°C, whereas the controlling kinetics change to step nucleation after approximately 25 hours at 1050°C, and 3 hours at 1250°C. The edge energy, ε, per unit length of ledge on a Nb (100) face is deduced from the application of equations (AI.11) and (AI.15) to be 1.5 x 10^{-11}
J/m at 1050°C, and 1.4 x 10^{-11} J/m at 1250°C. Bubbles growing under identical conditions in Nb containing 0.3, 1, and 2.07% Zr, are always limited by step-nucleation and do not exhibit surface diffusion kinetics at any time. The bubble size in these alloys is significantly smaller than that in pure Nb, but the number density is greater by a factor which varies between 4.5 and 8.5 depending on the amount of Zr present.

The application of equations (8.2) and (AIII.5) has revealed that 0.3% Zr initially increases ε to 6.3 x 10^{-11} J/m at 1050°C, whereas 1% Zr increases ε to 1.1 x 10^{-10} J/m. In Nb-2.07% Zr the edge energy was deduced to be 4.3 x 10^{-11} J/m at 1050°C. This is lower than found for the other alloys, but it is still substantially larger than the corresponding Nb value. This increase in the Nb edge energy when Zr is present can be interpreted in terms of the affinity of the solute for interstitial impurities - particularly Oxygen. The breakaway/re-saturation phenomenon which occurs in Nb-0.3% Zr and Nb-1% Zr after 15 hours at 1050°C, produces a terminal bubble size that corresponds to ε = 4.3 x 10^{-11} J/m. This reduction in ε to the level observed for Nb-2.07% Zr has been attributed to a segregation phenomenon which involves Zr-O defects. Vacancy drag induced segregation may also be a contributory - although small - effect.

Bubbles in Nb-1% Zr at 1250°C exhibit a dramatic size increase after approximately 2 hours, and they are often observed to have strain fields around them. Furthermore, an ordering phenomenon which involves interstitial impurities is found to occur at this temperature. The strain fields are unlikely to be caused by an excess pressure alone, and so it is suggested that the ordering process produces some kind of sub-oxide phase at the bubble surface, such that ε is reduced below the corresponding Nb value. Finally, the presence of large bubbles and their development with increasing time at temperature was discussed. A reduction in ε of some bubbles due to an early segregation phenomenon seems most likely to be responsible for their initial development. However, long range interactions due to non-spherical morphologies, and material anisotropy, may also be important.
1) Helium bubbles in Niobium and Nb-Zr alloys which contain up to 2.07%Zr in solid-solution, are faceted \{100\}/\{110\} polyhedra, or \{100\} cubes. These bubbles grow by a migration and coalescence mechanism during post-implantation annealing at temperatures between 950 and 1250°C.

2) Bubble mobility in Nb is limited by surface diffusion throughout anneals up to 100 hours at 950°C, but the control mechanism changes to ledge nucleation after approximately 25 hours at 1050°C, and 3 hours at 1250°C. The energy, $\varepsilon$, per unit length of ledge on a Niobium (100) facet is deduced to be $1.5 \times 10^{-11}$ J/m at 1050°C, and $1.4 \times 10^{-11}$ J/m at 1250°C.

3) The mobility of He bubbles in Nb-0.3%Zr, Nb-1%Zr, and Nb-2.07%Zr, at 1050°C is limited by ledge nucleation on the atomically flat facets of a bubble surface. For anneals up to 15 hours at this temperature $\varepsilon$ is $6.3 \times 10^{-11}$ J/m, and $1.1 \times 10^{-10}$ J/m, in Nb-0.3%Zr and Nb-1%Zr, respectively. For longer anneals $\varepsilon$ in both materials is reduced to $4.3 \times 10^{-11}$ J/m which corresponds to the value deduced for Nb-2.07%Zr at this temperature. Bubble mobility is also ledge nucleation limited in Nb-1%Zr at 950°C where $\varepsilon$ is $1 \times 10^{-10}$ J/m. However, although bubble migration in Nb-1%Zr is initially ledge nucleation limited with $\varepsilon = 6.0 \times 10^{-11}$ J/m at 1250°C, the characteristic bubble size dramatically increases after 2 hours such that a twenty-fold increase occurs within 40 hours. An ordering phenomenon involving interstitial impurities (particularly O) develops at this temperature, and the formation at bubble surfaces of a Nb-Zr-O sub-oxide phase having $\varepsilon \approx 1.4 \times 10^{-11}$ J/m seems most likely to be responsible for the breakaway of bubble size.

4) The presence of Zr in solid-solution therefore increases the Nb edge energy by a factor between 4 and 8. This increase occurs because Zr has a great affinity for interstitial...
impurities - especially Oxygen - and so it effectively cleanses bubble surfaces. Furthermore, it is suggested that the reduction of $\varepsilon$ to $4.3 \times 10^{-11}$ J/m in both Nb-0.3\%Zr and Nb-1\%Zr after about 15 hours at 1050°C, is related to the segregation of Zr-O defect clusters.

5) The parameters $Q_s$ and $D_o$ for Nb surface diffusion in the temperature range 950 to 1250°C, are deduced to be 332.8 kJ/mole and $1.4 \times 10^{-4}$ m$^2$/sec, respectively. The $Q_s$ value is much higher than anticipated because of O contamination of the bubble surfaces. In Nb-1\%Zr $D_o$ and $Q_s$ are $1.77 \times 10^{-5}$ m$^2$/sec and 178.39 kJ/mole, respectively, within the temperature range 900 to 1150°C provided the edge energy is approximately constant at $1 \times 10^{-10}$ J/m.

6) Bubbles in all these materials develop excess pressures during annealing. The over-pressure - the presence of which is demonstrated in Nb-1\%Zr - plays an important role in the development of $\{100\}$ cubes as annealing proceeds.

7) A simple analysis of the post-coalescence shape re-arrangement process, when limited by surface diffusion and ledge nucleation, has verified that bubble mobility in Nb-1\%Zr is indeed ledge nucleation limited. Furthermore, the presence of stepped and 'brick-shaped' $\{100\}$ bubbles can be explained in terms of the ledge nucleation limited kinetics and the excess pressure within the cavity. The edge energy, $\varepsilon$, is recognized to be the most important single parameter which determines whether surface diffusion or ledge nucleation limits shape re-arrangement and the mobility of $\{100\}$ cubic bubbles.

8) Finally, the presence of relatively few, but very large bubbles, which develop with increasing time at temperature in the Nb-Zr alloys, is thought to be due to a premature reduction in $\varepsilon$ (and therefore an increased mobility of these bubbles) due to a segregation phenomenon involving Zr-O complexes. Since Nb and its Zr containing alloys are anisotropic long range bubble interactions may exist and contribute to the development of these large bubbles.
APPENDIX I

THE MIGRATION AND COALESCE OF \{100\} BUBBLES LIMITED
BY SURFACE DIFFUSION

A - The bubble diffusion coefficient, \( D_{bs} \):

From random walk statistics the bubble diffusion coefficient is (183):

\[
D_{bs} = \frac{1}{6} \Gamma_b a_b^2 \quad \cdots \cdots \text{(AI.1)}
\]

where \( \Gamma_b \) is the bubble jump frequency, and \( a_b \) is the average jump distance. For a cubic bubble of dimension \( a \) the number of participating atoms per unit jump of cavity is \( 6a^2/a_s^2 \) (cf. Nichols (86) for spherical bubbles), where \( a_s \) is the average jump distance of a surface atom. If the surface atom jump frequency is \( \Gamma_s \), then

\[
\Gamma_b = \Gamma_s \frac{6a^2}{a_s^2}
\]

When the bubble moves a distance \( a_b \), then \( n^3/\Omega \) atoms must move the same distance, but in the opposite direction, so that

\[
a_b = a_s \frac{\Omega}{n^3}
\]

Since \( D_s = \frac{1}{\Omega} \Gamma_s a_s^2 \) - where \( D_s \) is the surface diffusion coefficient of the diffusing species - \( \Gamma_s \) can be eliminated from the above equations and equation (AI.1) can be rearranged to provide:

\[
D_{bs} = \frac{4\Gamma_s \Omega^2}{a_s^2 a} \quad \cdots \cdots \text{(AI.2)}
\]
The rigorous mathematical analyses presented by Gruber (91) and Baroody (92), for spherical bubbles, are based on the analogous problem of colloid coagulation as formulated by Chandrasekhar (89). The coalescence rate, $J_{ij}$, between bubbles containing $n_i$ and $n_j$ gas atoms can be expressed as (89, 91):

$$J_{ij} = 4\pi D_{ij} R_{ij} v_i v_j \left\{ 1 + \frac{R_{ij}}{(\pi D_{ij} t)^{1/2}} \right\}$$

Here $v_i$ and $v_j$ represent the number of bubbles per unit volume containing $n_i$ and $n_j$ gas atoms, respectively, $D_{ij}$ is the bubble diffusion coefficient such that $D_{ij} = D_i + D_j$ (89), and $R_{ij}$ is the interaction distance. If the average distance travelled by two bubbles relative to each other is large compared to the sum of their sizes then the second term in brackets in equation AI.3 can be neglected (89, 91). For a population of cubic bubbles which all have the same characteristic dimension $a$ (i.e. all bubbles have the size which is characteristic of the population produced by annealing for time $t$ at temperature $T$), then

$$D_i = D_j = D_b$$
$$v_i = v_j = v$$
$$R_{ij} = a$$

Thus equation AI.3 simplifies to:

$$J = 8\pi D_b a v^2$$

Each coalescence event reduces the number of bubbles per unit volume by one and so

$$J = -\frac{dv}{dt}$$

If the gas obeys the perfect gas laws then $PV = nRT$ where $V = a^3$ and
\( p = 4\gamma/a \{111\} \). (Here \( \gamma \) is the surface energy of the \( \{100\} \) planes). Hence

\[
n = \frac{4\gamma a^2}{kT}
\]

and

\[
nV = zm
\]

where \( m \) is the number of implanted gas atoms per unit volume, and \( z \) is the fraction of these actually contained within bubbles.

\[
\therefore \quad \nu = \frac{zmkT}{4\gamma a^2}
\]

Substituting equation AI.5 into equation AI.4, and equating with equation AI.6 gives:

\[
\frac{da}{dt} = \frac{\pi D_b zmkT}{\gamma}
\]

Substituting \( D_b = D_{bs} \) (equation AI.2) yields

\[
\frac{da}{dt} = \frac{4\pi D_s \Omega^2 zmkT}{\gamma a_s^2 a^4}
\]

Integrating this expression, and assuming the bubble size \( a_o \) at \( t=0 \) is approximately zero (ie. assuming \( a^5 = a_o^5 \)), gives

\[
a^5 \sim \frac{20\pi D_s \Omega^2 zmkT}{a_s^2 \gamma} \quad \ldots \ldots (AI.7)
\]

Hence cubic bubbles exhibit the same \( t^{0.2} \) dependence as spherical bubbles for surface diffusion kinetics. However, in Nb - Zr alloys most bubbles have cube dimensions smaller than 10 nm, and so the gas within them obeys Van der Waals equation rather than the perfect gas laws. For small bubbles the following simplified Van der Waals equation can be used with negligible error (73):

\[
P(V - nb) = nkT \quad \ldots \ldots (AI.8)
\]
where \( b = 4.48 \times 10^{-29} \text{ m}^3 \) (186). Using this equation in the above analysis modifies equation AI.5 to

\[
v = \frac{zm(kTt + hYb)}{hYb^3} \quad \text{.....(AI.9)}
\]

so that

\[
-\frac{dv}{dt} = \left\{ \frac{zmkT}{2Ya^3} + \frac{3zmb}{h} \right\} \cdot \frac{da}{dt} \quad \text{.....(AI.10)}
\]

If the initial bubble size is again assumed to be zero at \( t = 0 \) the relationship between bubble size, annealing time, and temperature, can be expressed as:

\[
F(a) \sim \frac{4\pi D_s Q^2 zmkTt}{a_s Y} \quad \text{.....(AI.11)}
\]

where

\[
F(a) = A - B
\]

\[
A = \left\{ \frac{M^5}{5} - 4.5QM^4 + 40Q^2M^3 - 160Q^3M^2 + 1536Q^5\ln(MkT) \right. \\
\left. + \frac{2048Q^6}{M} \right\}
\]

\[
B = (1536\ln(4kTQ) - 435.2)
\]

Here \( Q = \frac{Yb}{kT} \) and \( M = (a + 4Q) \).

Although this equation is complex it is amenable to computer manipulation and is used in chapter 8 to match some experimental data for Nb. A \( D_s \) value derived from the application of this equation is sensitive to the value of \( a_s \) which enters as a squared term. Throughout this work \( a_s = 1 \) nm has been assumed as typical for temperatures of 0.5 \( T_m \).
Consider the cubic bubble shown schematically in figure (AII) above. A ledge may be nucleated in the form of a 'pillbox' at the centre of a face (110), or as a quadrant emerging from a facet corner (119). Since the latter is the lower energy configuration, the activation energy needed to form a ledge nucleus of height \( h \), length \( L \), and having energy per unit length \( \varepsilon \), is (119):

\[
\Delta G = L\varepsilon + \frac{L^2 h}{\pi} \Delta G_v
\]  

where \( \Delta G_v \) is the free energy change per unit volume of material transferred from one side of the bubble to the other (110). If the bubble
retains its cubic shape $\Delta G_V = 0$, and the nucleation activation free energy $\Delta G^*$ for a nucleus of critical size $L^*$ is:

$$\Delta G^* = L^* \varepsilon$$

The critical size $L^*$ is shown in figure (AII) and equals $\pi a^2/8$. Once the ledge has reached this size it can reduce its total energy by advancing across the facet in the direction indicated. The nucleation frequency of critical size ledges is (110):

$$f = \frac{2D_s L^*}{a_s h^2} \exp \left(-\frac{\Delta G^*}{kT}\right)$$

Substituting for $\Delta G^*$ and $L^*$ gives

$$f = \frac{D_s \pi a}{a_s h^2} \exp \left(-\frac{\pi a \varepsilon}{2kT}\right) \quad ......(AII.2)$$

The bubble diffusion coefficient, $D_{bf}$, is again described by the random walk equation

$$D_{bf} = \Gamma_b a_b^2$$

In this case the bubble jump frequency, $\Gamma_b$, is equivalent to the ledge nucleation frequency (equation AII.2), and the jump distance, $a_b$, is the same as the ledge height $h$. Substituting for $\Gamma_b$ and $a_b$ provides:

$$D_{bf} = \frac{D_s \pi a}{6 a_s} \exp \left(-\frac{\pi a \varepsilon}{2kT}\right) \quad ......(AII.3)$$

---

**B - MIGRATION AND COALESCENCE**

An approximate relationship between the characteristic cube dimension $a$, the temperature $T$, and the annealing time $t$, can be deduced for ledge nucleation limited growth in a manner similar to that described in section B of
Appendix I. If the same assumptions are made the coalescence rate, \( J \), is again given by equation (AI.4), ie:

\[
J = 8 \pi D_b a \nu^2 = - \frac{d\nu}{dt} \quad \ldots \quad (AI.4)
\]

Since most bubbles in Nb-Zr alloys have cube dimensions below 10 nm, the simplified Van der Waals equation is used here to describe the gas in the bubbles. Hence, substituting equations (AI.9) and (AI.10) for \( \nu \) and \(-d\nu/dt\), respectively, and putting \( D_b = D_b^* \) (equation AII.3), then equation (AII.4) provides:

\[
4 \int_0^a \frac{a^4 \exp(\pi a \xi/2kT) \cdot \left\{ \frac{A}{a^3} \cdot \frac{\ln \left( \frac{a^3}{4} \right)}{a^4} \right\}}{(a^3 + 2b)^2} da = \int_0^t \frac{8 \pi^2 D_s \text{zm}}{6 a_s} \cdot dt
\]

where \( \Lambda = kT/2\gamma \). To define the limits to these integrals the bubble size is a after time \( t \), but the initial bubble size \( a_0 \) is assumed to be approximately zero at time \( t = 0 \).

If the substitution \( \omega = a\Lambda + 2b \) is made the left hand side may be integrated by parts, and the final expression is

\[
\left[ \begin{array}{ll}
\frac{a\Lambda + 3b}{(a\Lambda + 2b)^2} - \frac{a\Lambda + 4b}{(a\Lambda + 2b)^3} + \frac{2a\Lambda + 10b}{(a\Lambda + 2b)^4} \ldots \end{array} \right] \exp(Ka\Lambda)
\]

\[
= \left[ \frac{\pi^2 D_s \text{zm}}{6 a_s} \right] \int_0^t dt
\]

where \( K = (\pi \xi/2kTA) \).

Only the first three terms of the series solution are given on the left-hand side. However, the substitution of parameter values typical of Nb-1%Zr reveals that the series is dominated by the first term. Thus approximating the left-hand side to the first term of the series, and inserting the limits, gives
the simplified expression:

\[
\frac{1}{\Lambda} \left\{ \frac{(n\Lambda + 3b)}{(n\Lambda + 2b)^2} \cdot \exp(Ka\Lambda) - \frac{3}{h_b} \right\} \sim \frac{\pi^2 D_s \zeta}{3 \sigma_s}
\]

\ldots \ldots \ldots (AII.5)

C - SENSITIVITY TO PARAMETER VALUES

Both equation (AII.5) above, and equation (AI.11) in Appendix I, have been used to match experimental data to deduce either \( \varepsilon \) or \( D_s \). The best-fit to the data, and therefore the value of \( \varepsilon \) or \( D_s \) derived, is to some extent dependent on the choice of values for some of the parameters in these equations. To deduce \( D_s \) from the experimental Nb data using equation (AI.11) it is strictly necessary to vary the Van der Waals constant \( b \), the surface energy \( \gamma \), and the ad-atom jump distance \( a_s \), with temperature. In this work these parameters, and \( z \) the fraction of implanted He which actually forms bubbles, are assumed to be constant in the temperature range 950 to 1250°C, and are given in Table 16. Subsequently, \( b \), \( \gamma \), and \( a_s \), were varied in turn to gauge the sensitivity of the best-fit line to these parameters. Varying \( b \) arbitrarily between \( 2.0 \times 10^{-29} \text{ m}^3/\text{atom} \) and \( 6.0 \times 10^{-29} \text{ m}^3/\text{atom} \), and \( \gamma \) between \( 1000 \text{ mJ/m}^2 \) and \( 2000 \text{ mJ/m}^2 \), does not produce a significant change in the position of the theoretical line with respect to the experimental Nb and Nb-Zr data. However, line position is sensitive to \( a_s \) whose magnitude and variation with temperature is effectively unknown.

Equation (AI.11) for surface diffusion control is more sensitive to \( a_s \) than equation (AII.5) for ledge nucleation control, because it appears as a squared term in the denominator of the right-hand side. The positional change of the theoretical lines as a function of \( a_s \) is illustrated for Nb and Nb-15%Zr at 1050°C in figure AII.1. Hence the value of \( D_s \).
figure AII.1: The sensitivity of best-fit lines to $a_s$.
derived from applying equation AI.11 to Nb data at a particular temperature, is directly influenced by the choice of $a$. Reynolds and Beere (119) have used $a = 10 \text{ nm}$ for Cu at $0.75 T_m$, and Chen and Cost (113) assumed $a$ to be 10 times the ledge height - i.e., $3 \text{ nm}$ for a ledge one atomic diameter in height - in Al at $0.88 T_m$. The temperatures used in the present work represent $0.55 T_m$, or lower, and so there is some justification for assuming $a = 1 \text{ nm}$, and for maintaining a constant value throughout the temperature range. The parameter $z$ is unlikely to vary significantly with temperature because bubbles are undoubtedly nucleated during heating prior to achievement of the final temperature. This heating rate is similar for all final annealing temperatures, and so if $z$ is independent of the Zr concentration this parameter will be similar in all the materials. Thus, in conclusion, data derived from matching the Nb and Nb-Zr results is sensitive to $a$, but the value of $1 \text{ nm}$ assumed here is thought to be reasonable for the experimental conditions used - especially in view of values assumed by researchers in other materials at higher normalized temperatures.
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PUBLISHED PAPERS
A technique for the preparation of thin foils from regions near to a metal surface

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Abstract A novel technique is described for producing specimens for electron microscopy with thin regions adjacent to the original specimen surface. The technique involves the electropolishing of a disc specimen, one surface of which is masked with a heavy organic liquid. When the specimen is perforated the masking liquid also serves to isolate the thin areas from further electrochemical or chemical attack. The technique has been applied to studies of helium bubbles in niobium and Nb-1%Zr.

There are many investigations which require a transmission electron microscopy study of the near-surface region of metals. This is particularly true for irradiation damage and inert-gas diffusion studies of materials which have been irradiated in low-energy accelerators, where the region of interest is close to the surface.

The technique most often used to produce foils from surface layers has been to back-thin a foil (Eyre and Bullough 1967) in a pTFE holder (Briers et al 1964) with the surface protected by a masking lacquer. However, this technique rarely gives consistent protection for the metal surface in the region of electron-transparent foil adjacent to the perforation, particularly with hydrofluoric acid electrolytes.

We needed to produce foils from niobium and niobium-zirconium alloys which had been irradiated with helium ions and then annealed to produce bubbles. The bubble zone was only about 600 nm in extent, starting about 200 nm below the specimen surface. The outer 300 nm were removed by repeated anodic oxidation and stripping in the way described by Pawel and Lundy (1964). The electrolyte conventionally used for electropolishing niobium is 10% H F, 90% H2SO4 (Goodhew 1973) and no lacquer could be found that would protect the ion-implanted region around the foil perforation. The pTFE holder technique combined with a light source and photocell can be used to switch off the electropolishing current as soon as a very small perforation has formed, so that the time available for the electrolyte to penetrate between the foil and the lacquer is minimised. However, even with these precautions the success rate is too low to be of practical use.

Consequently, a new technique has been developed that not only can produce consistently protected foils but also switches off the current and chemically isolates the specimen from the electrolyte when the perforation has reached the required size. The technique is also suitable for preparing specimens for transmission electron microscopy in general, and has the advantage of being automatic, no continuous

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observation of the progress of electropolishing being necessary, and no expensive and cumbersome electro-optical system is needed. It is, however, advisable to extract the specimen soon after thinning or staining may occur.

Figure 1 The specimen environment in the single-sided electropolishing cell. The stainless steel tube anode A seals the 3 mm disc specimen into the PTFE electrolyte tank. The lower surface of the specimen is protected by the inert liquid L.

The method is illustrated in figure 1. The surface to be protected is in contact with an organic liquid which is at a positive pressure with respect to the electrolyte, the magnitude of this pressure being controlled by the 'head' of liquid. The liquid must satisfy the following conditions:

(i) it must be immiscible with the electrolyte;
(ii) it must not react significantly with the electrolyte;
(iii) it must be an electrical non-conductor;
(iv) it must have a higher density than the electrolyte, yet a low viscosity;
(v) it must not react with the specimen.

If the above conditions are satisfied, the liquid will flow through the perforation in the foil, cover the specimen and isolate the specimen both chemically and electrically from the electrolyte. This is particularly useful for electrolytes which continue to attack the specimen when the current is switched off. The final size of the perforation will be a function of the surface tension between the liquids and the pressure differential between the liquid and the electrolyte; the larger the head of liquid the smaller the perforation.

For niobium, the electrolyte (10% HF, 90% H2SO4) is best used at a temperature of 60°C and it must be stirred if a good polish is to be obtained in a reasonable time. For Nb-1% Zr we have found that 10% HF, 13% HNO3, 77% H2SO4 is a more effective electrolyte, used at 65°C. These electrolytes have a high density (about 1.8) and therefore the protective liquid must have a higher density and for best protection a large surface tension. The liquid used is 1, 2 dibromoethane (ethylene dibromide).

The apparatus used for this technique is illustrated in figure 2. The holder is made of PTFE and is approximately 45 mm in diameter and 64 mm high, the internal diameter being about 22 mm. The geometry in the region of the specimen (see figure 1) is critical for niobium. If the edge thickness is much more than 0.25 mm, stable bubbles will form as the flow of electrolyte produced by the stirrer does not reach the specimen surface if this dimension is too large. If it is too small, there may not be sufficient strength to resist the force necessary to produce a leak-tight seal between the specimen and the metal tube, this tube being spring-loaded against the face that is to be protected. The tube consists of an end-piece which contacts the specimen made of stainless steel, of 3 mm od and 2 mm id (for a 3 mm disc specimen) and about 5 mm long, which is soldered into a copper tube which acts as a heat sink. It is important that the organic liquid is at as low a temperature as possible. Even though at perforation the electrolyte and the liquid are in contact, and therefore presumably at the same temperature at the liquid interface, early difficulties with this technique were caused by the liquid being hotter than absolutely necessary. The high electrolyte temperature gives a rapid polish of high quality, presumably because the lower viscosity at these temperatures gives the electrolyte the necessary mobility needed to sweep bubbles from the surface being polished.

To load a specimen the holder is turned upside-down, the disc is placed in position and the metal tube is then spring-loaded against the specimen. The tube is filled with liquid, and care is taken so that an air lock is not formed (wetting the tube with methanol helps to prevent bubbles from being trapped in the tube). If the liquid leaks out, the spring tension can be increased, as the disc may not be flat (some of the specimens used in our study were only 0.05 mm thick). If this does not cure the leak, then either the specimen or the tube end is damaged. When a reasonably leak-tight joint has been obtained a plastic tube and funnel are connected and filled with liquid. The holder can then be inverted and fixed to a retort stand, the funnel being clamped in the appropriate position to give the required 'head' of liquid.

The technique was developed specifically for the preparation of niobium discs but has also been used for the preparation of iron foils, using a chromic acid/acetic acid electrolyte.
Apparatus and techniques

(Goodhew 1973) and chloroform as the inert liquid. The method is somewhat simpler for iron as neither stirring or heating is required.

For niobium and its alloys the most critical part of the technique is the stirring of the electrolyte. The polishing current is very dependent upon the efficiency with which bubbles can be swept away from the surface by the flow of electrolyte, but excessive stirring must be avoided as it can jeopardise the protection of the foil after perforation and will increase the amount of liquid needed to isolate the specimen from the electrolyte. A stirrer rotating at about 100 rev min⁻¹ a few millimetres away from the surface of the specimen has been found most suitable. The technique has now been used by a variety of workers over a period of five years and is consistently successful. An example of a foil containing helium bubbles, thinned using this technique, is shown in figure 3.

Figure 3 A thin foil prepared from a region 250 nm below the surface of an irradiated Nb-1% Zr specimen, showing helium bubbles.

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THE GROWTH OF HELIUM BUBBLES IN NIOBIUM AND Nb–1% Zr

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Helium bubbles have been precipitated in niobium and Nb–1% Zr by room-temperature irradiation with α-particles followed by isothermal annealing at 1050°C. It has been established that the bubbles grow by a migration and coalescence mechanism. After long annealing times all the bubbles are strongly faceted but many are extremely elongated. From the growth rates of the bubble populations it is possible to establish that the rate-controlling mechanism is surface diffusion for small bubbles and facet nucleation for larger bubbles. A model for the growth of elongated bubbles by facet nucleation is developed and from it the energy of an edge on a \{100\} facet can be estimated as $1.2 \times 10^{-11}$ J/m for niobium. In the Nb–1% Zr alloy the edge energy is at least four times greater.

1. Introduction

It is well known that helium introduced interstitially in metal lattices can be induced to precipitate as bubbles [1,2]. Even in the absence of a continuous supply of helium the bubbles may grow by a process of migration and coalescence [1]. The equilibrium size and shape of a bubble is determined by the balance between the pressure of the helium contained within it and the surface tension of the crystal surfaces bounding it. The rate of growth of the bubbles in a particular bubble population depends on the mechanism by which the bubbles migrate. In the case of small bubbles migrating at random under a net zero driving force in niobium the migration has been shown to be controlled initially by surface diffusion around the inside of the bubble [3]. Further work has shown [4] that after longer times (i.e. for larger bubbles) the migration and hence growth may be controlled by the nucleation of atomic steps on the faceted surface of the bubble, as has been demonstrated for some fcc metals [5,6].

The analysis of bubble growth data is extremely complex unless the bubble population can be assumed to have a regular size distribution and each bubble is approximately equiaxed. For the work quoted above, including our own work on small bubbles in niobium, these approximations have generally been realistic and the growth of the bubbles has been amenable to treat-
ment by standard techniques [7,8]. However, we have recently found that after longer annealing times in Nb–1% Zr the bubble distribution becomes multimodal and many bubbles become elongated. Since both these effects complicate the interpretation of bubble growth data we have examined the bubble shapes and their size distribution more carefully. Although elongated bubbles have been reported previously in vanadium [9] no explanation for their occurrence has been put forward. We will consider this point in our discussion.

2. Experimental

Helium was introduced into thin sheets of niobium and Nb–1% Zr by ion implantation. Sequential irradiation at four energies (50, 100, 140 and 220 keV) gave a very nearly uniform concentration of $5 \times 10^{26}$ atoms/m$^3$ throughout a region 600 nm in depth. After irradiation at room temperature the sheets were annealed in vacuo at temperatures between 850 and 1350°C to precipitate and grow the bubbles. Thin foils for electron microscopy were prepared by a special technique designed to ensure that the thin part of the specimen was in the centre of the helium-implanted region [10]. The bubbles were photographed slightly under-focus in a JEM 100B microscope operating at 100 kV.

3. Observations and results

Helium bubbles in both pure niobium and the alloy are faceted from very small sizes. Fig. 1 shows a typical field of small bubbles in Nb–1% Zr and fig. 2 indicates the distribution of bubble sizes found in this specimen. From data such as these both we [3] and other workers [5,6] have determined by a “mean bubble diameter” to characterize the bubble population.

After longer annealing times, however, the bubble population is significantly different. Fig. 3 shows a typical micrograph from Nb–1% Zr after 8 h at 1050°C. Some of the bubbles are very much larger than the general population, as is borne out by the histogram shown in fig. 4. In this histogram the mean bubble diameter for the large bubbles is the average of the three dimensions of the rectangular parallelepiped, each corrected for foreshortening in the micrograph. Clearly the
larger bubbles have broken away from the main distribution and appear to have undergone accelerated growth.

The shapes of the bubbles also change as annealing (and bubble migration) proceeds. Small bubbles (cube side, $a < 3.5$ nm) are generally 18-sided with $\{110\}$ and $\{100\}$ facets developed but after longer times the $\{100\}$ facets dominate until the brick-shaped bubbles with $\{100\}$ faces are formed. At this stage only an occasional small $\{110\}$ facet remains. The major axis
of the “brick” may be any of the \(\{100\}\) and all three orientations are generally seen within a single grain (e.g. fig. 5). Aspects ratios greater than 4 to 1 have frequently been seen. A further frequent observation is that of bubbles with complex shapes composed of many facets, usually \(\{100\}\) but very occasionally with bevelling on \(\{110\}\) at the corners. An example is shown in fig. 6. Since this sort of shape presents a very large surface area compared to a simple cube of the same volume it is presumably not the equilibrium shape but must indicate that there are obstacles to the attainment of equilibrium.

It is of interest to compare the growth rates of bubbles in pure niobium and the alloy at the same temperature. In fig. 7 is plotted the modal bubble size versus annealing time at 1050°C for both pure metal and alloy. Although we do not yet have data for very long annealing times it appears that in both materials the bubbles reach a size at which they scarcely grow. However, in the pure metal this is preceded by a period during which \(\log(\text{size})\) is linear with \(\log(\text{time})\): such a period is not apparent in the alloy.

4. Discussion

Qualitatively a number of points are immediately evident from these results.

(a) The bubbles have a strong tendency to facet, although the dominant facets vary as the bubbles grow.

(b) The addition of 1% Zr decreases both the mean bubble size at each annealing time and the bubble size at which growth essentially stops.

(c) In pure niobium there appears to be a change of rate-controlling process, after \(~20\) h at 1050°C at a bubble size of \(~20\) nm.

(d) For large bubbles the equilibrium shape is rarely reached at 1050°C.

We have previously shown that the straight section of the bubble growth plot in fig. 7 is consistent with a surface diffusion-controlled migration and coalescence growth mechanism in niobium [3]. However, this mechanism is clearly not the limiting process in Nb–1% Zr at 1050°C. Work on bubbles in fcc metals has shown [5,6,11] that the rate-controlling step may be the nucleation of ledges on the bubble facets. Since the bubbles found in this study, and in other bcc metals [9,12], are frequently bounded by a smaller number of large facets than bubbles in fcc metals it seems likely that facet-nucleation-limited growth will occur. The general form of such growth kinetics gives a high growth rate at small bubble sizes, decreasing to an almost negligible rate as the bubble size increases [6], which is precisely what we observe in our specimens. We have therefore developed a general analysis of the migration behaviour of an asymmetric faceted bubble limited by facet nucleation. This is then compared with our bubble data for both niobium and Nb–1% Zr in order to deduce limits on the controlling parameters.

At 1050°C (= 0.48 \(T_m\)) the equilibrium vacancy concentration in the lattice is relatively low and despite the likely high excess gas pressure in the larger bubbles their rate of approach to equilibrium volume after coalescence, as calculated for example as suggested by Greenwood et al. [13], is effectively zero on the time scale of our experiments. Consequently, the following analysis considers migration and shape changes occurring only by the transport of atoms around the inside of the bubble.

Consider a bubble in the shape of a rectangular prism with edges \(a, b\) and \(c\), in general unequal (fig. 8). In the absence of a bulk vacancy flux face 1 can migrate only by transfer of atoms from faces 2 and 3. Equivalently face 4 can be considered to migrate by transfer of atoms from faces 5 and 6. Considering only face 1 it can easily be shown [11] that if the bubble volume is conserved the energy change per unit volume of material transferred from face 2 is, ignoring second order terms,

\[
\Delta G_{v}^{21} = \frac{-2\gamma(a - b)}{ab},
\]

where \(\gamma\) is the surface energy and surface stress terms can be ignored since the number of surface atoms per

\[\text{Fig. 8. Model for an elongated bubble faceted on } \{100\}\.]
unit area is unchanged. Similarly, for the transfer of atoms from face 3

$$\Delta G^{31} = -\frac{2\gamma(a - c)}{ac}.$$  \hspace{1cm} (2)

Now the nucleation of a step on face 1 could occur from a “pillbox” in the centre of the face or from a quadrant emerging from one corner. The latter is generally the lower energy configuration and therefore, following Beere and Reynolds [11], we write the activation energy to form a nucleus as

$$\Delta G = Le + \frac{L^2h}{\pi} \Delta G_v,$$  \hspace{1cm} (3)

where \( L \) is the length of the perimeter of the nucleus, \( e \) is the energy per unit length of the step of height \( h \), and \( \Delta G_v \) is the change in energy per unit volume of material transferred. Differentiating with respect to \( L \) and equating \( \frac{d\Delta G}{dL} \) to zero we find that the critical nucleus size and energy are

$$L^* = -\frac{e\pi}{2h\Delta G_v}$$  \hspace{1cm} (4)

and

$$\Delta G^* = -\frac{e^2\pi}{4h\Delta G_v}.$$  \hspace{1cm} (5)

Now in the absence of a temperature or stress gradient the total driving force arises only from the surface area reduction [eqs. (1) and (2)] and must drive the nucleation of steps on faces 1, 2 and 3. To a first approximation the energy available for step nucleation on face 1 is thus

$$\Delta G_v = \frac{\Delta G^{31} + \Delta G^{31}}{3} = -\frac{2\gamma[a - b + a - c]}{3a \left[\frac{b}{c} + \frac{a - c}{b}\right]},$$

which we will write for simplicity as

$$\Delta G_v = -2\gamma S/3a,$$  \hspace{1cm} (6)

where

$$S = \frac{a - b}{b} + \frac{a - c}{c}.$$  \hspace{1cm}

Using this value of \( \Delta G_v \) in eqs. (4) and (5) we derive

$$L^* = 3e\pi n/4\gamma hS,$$  \hspace{1cm} (7)

and

$$\Delta G^* = 3e^2\pi n/8\gamma hS.$$  \hspace{1cm} (8)

Now we can estimate the value of \( L^* \), the critical nucleus size, from reasonable values of \( \gamma, e, h \) and \( S \). For niobium the bulk surface energy has been measured as 2.1 J/m\(^2\) [14] and simple consideration of a Wulff plot would suggest that if bubbles facet entirely on \( \{100\} \) planes the surface energy of this plane should be \( \approx \)30% lower than this; we have therefore used a value of 1.5 J/m\(^2\). The edge energy, \( e \), has previously been found to lie between \( 10^{-10} \) and \( 10^{-11} \) J/m for copper and gold [15] and an elementary calculation for bcc niobium relating it to the surface energy via numbers of “broken bonds” gives an answer of the same magnitude. We have taken \( h \), the step height on a \( \{100\} \) face, to be half the lattice parameter (i.e. \( h = 0.165 \) nm). The ratio \( S \) will be zero for a cubic bubble for which \( a = b = c \). At this point our treatment must diverge from Beere and Reynolds since they considered cases where \( a \sim b \sim c \) whereas our simplest and least extreme case is that of two identical cubic bubbles, side \( b \), which coalesce to give a brick-shaped bubble for which \( a = 2b = 2c \). For this configuration \( S = 2 \) and \( 0.1 < L^* < b \).

It then seems reasonable to use expression (8) for the critical nucleation energy. However, if \( S \) were smaller then \( L^* \) would be higher; for example, if \( a = 1.1b = 1.1c \), then \( S = 0.2 \) and \( 0.5b < L^* < b \) and it might be more reasonable to use the minimum bubble dimension to define the stable nucleus, i.e. \( L^* = \pi b/2 \). Since we wish to apply this analysis both to approximately cubic bubbles (low driving force) and to very elongated bubbles (high driving force) we shall develop models based on both criteria for \( L^* \).

4.1. High driving force

The nucleation frequency of steps of length \( L^* \) on face 1 will be given by [5]

$$f^{(1)} = \frac{2D_sL^*}{\alpha}\exp \left[ \frac{-\Delta G^*}{kT} \right],$$  \hspace{1cm} (9)

where \( D_s \) is the surface diffusion coefficient and \( \alpha \) is the unit jump distance of the surface diffusing species. Using the values of \( L^* \) and \( \Delta G^* \) given by eqs. (7) and (8) we obtain

$$f^{(1)} = \frac{3D_s\alpha n}{2\gamma h^3\alpha}\exp \left[ \frac{-3e^2\pi n}{8\gamma hS\alpha kT} \right].$$  \hspace{1cm} (10)

The bubble diffusion coefficient \( D_b \) for a bubble
moving at random in a cubic crystal is

\[ D_b = \frac{1}{6} \alpha a^2, \]

where \( \alpha \) is the jump distance, which in this case is equal to the step height \( h \). Hence

\[ D_b(\text{facet}) = \frac{D_b \alpha n}{4 \gamma h S \alpha} \exp \left( -\frac{3 \alpha^2 \alpha n}{8 \gamma h S kT} \right). \]  

(11)

4.2. Low driving force

If the bubble is nearly cubic and \( S \) is small then \( L^* = \frac{\pi b}{2} \) and \( \Delta G^* \) is given by

\[ \Delta G^* = \frac{\pi be}{2} + \frac{\pi b^2 h \Delta G_v}{4} \]

or

\[ \Delta G^* = \frac{\pi be}{2} \left( \frac{\epsilon - b h y S}{3a} \right). \]  

(12)

Then following the same analysis as in the previous section

\[ D_b(\text{facet}) = \frac{D_b \alpha \pi}{6 \gamma h S \alpha} \exp \left( -\frac{nb}{2kT} \left( \frac{\epsilon - b h y S}{3a} \right) \right). \]  

(13)

4.3. Diffusion-limited case

It will be useful to compare the bubble diffusion coefficients predicted by facet nucleation limits with those predicted if surface diffusion is rate-controlling. The appropriate equation for a cubic bubble is

\[ D_b(\text{diffusion}) = \frac{4 D_b \Omega^2}{a^2 \alpha^4}, \]  

(14)

where \( \Omega \) is the atomic volume, which differs from that derived for a spherical bubble by, for example, Nichols [8] only in the geometric constant.

We can use eqs. (13) and (14) to derive a ratio which indicates the relative magnitude of the bubble mobilities due to the alternative rate-controlling processes. For approximately cubic bubbles (low driving force)

\[ R = \frac{D_b(\text{facet})}{D_b(\text{diffusion})} = \frac{\pi a^4 b \alpha}{24 \Omega^2} \exp \left( -\frac{nb}{2kT} \left( \frac{\epsilon - b h y S}{3a} \right) \right). \]  

(15)

which reduces, for cubic bubbles, to

\[ R = \frac{\pi a^4 b \alpha}{24 \Omega^2} \exp \left( -\frac{nb \epsilon}{2kT} \right). \]  

(16)

Now at 1050°C, fig. 7 indicates that the rate-controlling mechanism in pure niobium changes from surface diffusion (linear portion) to facet nucleation (flattening out at a bubble size of ~20 nm. If we substitute \( R = 1, \ a = 20 \) nm, \( \alpha = 1 \) nm and \( \Omega = 1.8 \times 10^{-25} \text{ m}^3 \) into eq. (15) we can deduce a ledge energy of \( \epsilon = 1.2 \times 10^{-11} \) J/nm, which is in good agreement with the estimated value.

We can also say that in the Nb–1% Zr alloy surface diffusion does not seem to control the growth even for bubble sizes as small as 2 nm. If we therefore say \( R < 1 \) for \( a = 2 \) nm we can conclude that \( \epsilon > 5.5 \times 10^{-11} \) J/nm. The effect of the Zr in the alloy is thus to increase the edge energy by a factor of at least four.

We can corroborate this estimate of edge energy for the alloy by considering the stability of brick-shaped bubbles. The velocity of face 1, limited by facet nucleation under a high driving force, will be

\[ \nu(1) = f(1) \frac{h}{\gamma S}, \]

which, from eq. (10) implies

\[ \nu(1) = \frac{3 D_b \alpha \pi}{2 \gamma h^2 S \alpha} \exp \left( -\frac{3 \alpha^2 \alpha n}{8 \gamma h S kT} \right). \]  

(17)

Since bubbles 10 × 10 × 40 nm are observed to be stable in our experiments we can deduce that for these bubbles \( \nu(1) < 10^{-13} \text{ m/s} \). Using the values of \( \gamma \) and \( h \) discussed above, with \( S = 6 \) we find that at 1050°C

\[ 10^{-13} > 7.7 \times 10^{13} e B_k \exp(-1.7 \times 10^{11} e^2). \]  

(18)

We have previously determined that the surface diffusion coefficient at 1050°C in niobium and Nb–1% Zr lies in the range \( 10^{-12} < D_s < 10^{-11} \text{ m}^2/\text{s}. \) [4]. In order to satisfy the inequality of eq. (18), \( \epsilon \) must lie in or above the range \( 8 \times 10^{-11} < \epsilon < 13 \times 10^{-11} \) J/m. This is in quite good agreement with the result deduced earlier.

5. Origin of stepped and elongated bubbles

The same facet-nucleation-limit which effectively prevents an elongated bubble from changing its shape to a cube will also inhibit the removal of all but the
smallest steps on a bubble surface (fig. 6). It seems most probable that both stepped and elongated bubbles arise from the coalescence of smaller bubbles - the new large bubbles retaining effectively the shapes they have on coalescence. This accounts for the existence of bubbles with widely, but randomly, varying aspect ratios. Small steps, with locally large effective values of $S$, will be able to nucleate ledges and thus will "anneal out", leaving the larger facets smooth. Since the facet nucleation mechanism is extremely sensitive to bubble size the larger bubbles must be essentially immobile. They will grow by coalescing with the more mobile small bubbles which collide with them. Although many bubbles lie on dislocation lines there is no evidence that dislocations channel small bubbles towards the larger ones. There is also no evidence of a denuded zone around each large bubble. It is thus still not clear why the biggest bubbles grow to such a size, since they must result from the coalescence of several hundred bubbles of the modal size. Our investigation is continuing in an attempt to determine the role of the Zr and that of the interstitial impurities (C, O and N) in controlling bubble migration.

6. Conclusions

(1) The behaviour of helium bubbles in Nb–1% Zr is distinctly different from that of those in niobium at 1050°C. The initial bubble size is smaller in the alloy but the mechanism of growth is still migration and coalescence.

(2) Bubble migration in niobium is initially controlled by surface diffusion but facet nucleation becomes dominant at larger bubble sizes.

(3) Bubble migration in Nb–1% Zr is controlled by facet nucleation. At 1050°C this is so sensitive to bubble size that stepped and elongated bubbles form; these cannot reach a lower energy symmetrical shape within $10^8$–$10^9$ s.

(4) It is possible to estimate the edge energy $e$ of a step on a (100) facet as $1.2 \times 10^{-11}$ J/m for niobium.

(5) The effect of the 1% zirconium addition is to raise $e$ to at least $5.5 \times 10^{-11}$ J/m. A second estimate, based on the stability of elongated bubbles, gives $e > 8 \times 10^{-11}$ J/m.

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LETTERS TO THE EDITORS — LETTRES AUX REDACTEURS

BUBBLES AND VOIDS WITH RINGED IMAGES

In the course of a transmission electron microscope study of helium bubble behaviour in niobium alloys we have frequently observed bubbles with two apparently concentric images. An example is shown in fig. 1 and this 'ringed bubble' contrast is displayed by typically 15% of the bubbles in each field of view. Examination of published micrographs of bubbles and voids in the open literature reveals that the appropriate conditions of resolution, contrast and reproduction which make these images visible are rarely met. However we have noticed in two recent publications clear examples of voids showing this type of contrast in austenitic stainless steel [1] and niobium [2].

In all the cases mentioned above the irradiation and heat-treatment required to nucleate and grow the voids or bubbles was carried out on bulk specimens prior to thinning for examination in the TEM. We would therefore expect that some bubbles in any field of view would intersect one or other of the foil surfaces. If it is possible to establish that ringed bubbles are those which intersect a foil surface then it would be possible to measure bubble densities without needing to determine local foil thickness, which would represent a great saving in experimental effort. Mean bubble size (e.g. diameter) could be determined from those bubbles which do not intersect a surface; subsequently bubble density could be determined by counting the number of ringed bubbles per unit area, dividing by two to avoid counting both surfaces and dividing by the mean bubble size (e.g. ref. [3]).

We have examined specimens of Nb-1%Zr by TEM and high resolution SEM, using a JEOL 100C TEMSCAN microscope in order to establish whether those bubbles with ringed images when viewed by TEM were those which appeared to intersect the foil surface when viewed by SEM. We took transmission micrographs from an area containing several ringed bubbles and some easily identifiable dirt particles, recorded an SEM micrograph from its upper surface, removed the specimen from the microscope and turned it over and finally relocated the same field and recorded a further SEM micrograph from its other side. A typical set of micrographs is shown in fig. 2.

It can be seen quite readily that each ringed bubble corresponds to a surface defect on one or other foil surface. Unfortunately even with an SEM resolution of about 3 nm it is not possible to record accurately the shapes of surface features in the size range 5—30 nm but there can be no doubt that the features seen in the SEM micrographs are the dimples caused by bubbles intersecting the foil surface. Several bubbles in fig. 2 are labelled to make the correspondence between TEM and SEM images absolutely clear.

It is of interest to consider the origin of the ringed
Fig. 2. The same area of a foil of Nb-1%Zr containing bubbles, viewed from both sides by TEM (a and b) and SEM (c and d). Ringed bubbles A and D appear only on one side of the foil (c), while B and C appear on the other (d). Bubbles such as E and F, without ringed images, appear on neither scanning micrograph.
contrast, in order to assess whether there are any conditions in which bubbles intersecting the surface would not show this distinctive effect. It has been suggested [4] that the effect arises from the bursting of bubbles containing a high gas pressure, either through local deformation or by differential electropolishing around a large gas bubble created in the electrolyte. However, neither of these mechanisms should lead to the type of contrast seen in fig. 1. In addition, the fact that ringed contrast is also seen around voids [1,2] effectively eliminates any mechanism involving the gas pressure.

A more probable explanation for the ringed contrast is the formation of a thin oxide film on the surface of the foil immediately after electropolishing. Since electropolishing is generally carried out at temperatures where surface diffusion is extremely slow any void or bubble which intersects a foil surface will retain its shape indefinitely. A thin oxide layer will therefore provide a shell of uniform thickness lining the inside of the bubble. Since voids and bubbles are usually studied using kinematical diffraction conditions where strain contrast is essentially invisible, the image results from the electron density difference between the void or bubble and its matrix. Micrographs are usually taken with slight underfocus to enhance bubble contrast by outlining the projection of the bubble with a dark fringe. In such conditions we would expect an oxide-lined surface bubble, as illustrated for example in fig. 3, to give rise to an inner image similar to that from a normal bubble. Since there is generally a considerable density difference between oxide and metal ($\rho_{\text{metal}} \approx 2 \times \rho_{\text{oxide}}$ for niobium) we would expect a similar image to arise from the oxide/metal interface. Thus in fig. 1 we see that both inner and outer images show a dark fringe. Similar effects should; and do, occur for other orientations.

![Fig. 3](image-url)

**Fig. 3.** A schematic illustration of a foil containing a surface bubble lined with oxide and a normal bubble.

The distance between the inner and outer dark fringes of a cuboidal bubble viewed along a (100) direction (as in fig. 1) should represent the oxide thickness. In our specimens, whatever the bubble size, this thickness is in the range 3–4 nm. This is in good agreement with the range of thicknesses deduced by Cabrera and Mott [5] for the first rapidly grown very thin film oxide on most metals (2–10 nm).

There is thus substantial evidence that ringed bubbles are those which have intersected the surface and have been lined with a stable oxide film of uniform thickness. Since neither the inner or outer fringe of the double image is likely to correspond exactly with the original bubble surface we should clearly eliminate ringed bubbles for measurement of mean bubble size. However we should consider whether ringed bubbles or voids can be used, as suggested by Rosolowski [6], for pore density measurement. The main reservations to this approach must be

i) the doubtful identification of bubbles or voids as ringed when their dimensions are of the order of twice the oxide thickness or less;

ii) similar problems of identifying very shallow bubble remnants or small corners truncated from, for example, cubes viewed along (111); and

iii) the possibility of the smallest surface dimples, arising from small bubbles, healing by surface diffusion.

Our view is that this technique can only be used for pores whose size distribution includes only a small percentage with dimensions less than twice the oxide thickness. Specific grains in which faceted bubbles are orientated so that they expose corners to the foil surface should be avoided.

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Irregular helium bubbles in niobium alloys

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SUMMARY

Helium bubbles have been produced in niobium-1% Zr by ion implantation and their growth has been studied by transmission electron microscopy of annealed specimens. Bubbles are normally faceted and develop from tetrakaidodecahedra at short times to cuboids bounded by {100} faces after long annealing periods. This behaviour, together with the observation of steps on the faces of many bubbles, is accounted for in terms of competition between the conditions necessary for thermodynamic equilibrium and the kinetics of bubble motion. The larger bubbles must contain an excess gas pressure.

1. INTRODUCTION

An important criterion in the choice of first wall material for controlled-thermonuclear reactors (CTR) is the long-term effect of radiation damage on physical and mechanical properties. One of the more subtle effects is the production of helium within the wall by transmutation processes. The gas has negligible solubility (Rimmer & Cottrell, 1957) and precipitates as bubbles which contribute to swelling and embrittle grain boundaries. Candidate wall materials are stainless steels, refractory metals, or refractory metal alloys. We have investigated the bubble growth phenomenon in Nb-1% Zr using α-particle irradiation and subsequent vacuum annealing. As well as appearing in a recent design (Thomassen et al., 1976) this alloy is interesting because Zr is produced by transmutation of Nb under CTR conditions. For example, an initially pure Nb first wall will contain ~4% Zr after thirty years operation at a neutron loading of 1 MW m⁻² per annum.

Inert gas bubbles in metals grow by a migration and coalescence process (Barnes & Mazey, 1963), but the growth rate of a given population is determined by atomic processes occurring at the bubble surface. Furthermore, the equilibrium size and shape of a bubble is determined by the balance between the pressure within it and the surface energy of the crystal surfaces bounding it. During our investigations, we have observed numerous peculiarities in bubble shapes which are related to the growth mechanism and controlling kinetics. Detailed considerations of these shapes suggest that bubbles contain an excess gas pressure and are not at equilibrium.

2. EXPERIMENTAL

Helium was introduced into annealed 25 μm foils of Nb–1% Zr by sequential implantations at 220, 140, 100 and 50 keV nominally at room temperature. A 0022-2720/79/0500-0055 $02.00 © 1979 The Royal Microscopical Society
uniform He concentration of 1 at% was produced at all depths between 200 and 800 nm from the implanted surface. The number of He atoms introduced is in excess of any concentration expected from transmutation under CTR conditions. It does, however, provide a high bubble density after annealing, minimizing interpretation difficulties encountered when studying the bubble growth phenomenon from size measurements.

The irradiated foils were subsequently wrapped in niobium foil and annealed at 1050°C in a dynamic vacuum better than 67 µPa for times up to 100 h. This treatment precipitates \(~10^{23}\) bubbles/m\(^3\) which remain small (<10 nm) even after 100 h annealing. Finally, transmission electron microscopy samples were prepared from the helium implanted region using a special technique (Aitken et al., 1978). These samples were analysed in a JEM 100B microscope operating at 100 kV, using kinematical diffraction conditions to investigate bubble shape changes as a function of time at temperature. All images were recorded about 0.5 µm under focus.

3. RESULTS

Helium bubbles formed during post-implantation annealing of Nb-1 at% Zr at 1050°C are very small but are distinctly faceted irrespective of annealing time. The modal bubble size after 100 h is only 6.5 nm. At short annealing times (up to approximately 8 h) the bubbles appear as regular hexagons when viewed in [111], whilst eight-sided polygons are observed in [100] (Fig. 1) and [110]. The bubble shape is an eighteen-sided tetrakaidecahedron composed of six \{100\} and twelve \{110\}.

For intermediate annealing times—between 8 and 25 h—a large proportion of bubbles lose their \{110\} facets and become \{100\} cubes. At this stage a few bubbles

![Fig. 1. Bubbles faceted on \{100\} and \{110\} planes after 8 h at 1050°C. Beam direction [001].](image-url)
Irregular helium bubbles in niobium alloys

show slight elongation along \( \langle 100 \rangle \). Beyond 25 h a more dramatic effect is observed. The majority of bubbles have become either \( \langle 100 \rangle \) cubes or rectangular parallelepipeds ('brick shaped' with \( a \neq b \neq c \)) bounded by \( \{100\} \) as illustrated by Fig. 2. Some bubbles only deviate slightly from perfect cubes but many have aspect ratios greater than four. These ratios vary significantly within the same grain and the long axes of the bubbles appear to be equally distributed among the \( \langle 100 \rangle \).

Many bubbles show shape peculiarities apart from simple elongation. Some—for example, bubble B in Fig. 3—show distinct surface steps running from one side of the face to the other in \( \langle 100 \rangle \) directions. The planes comprising these steps are generally \( \{100\} \) but occasionally \( \{100\}/\{110\} \) combinations have been observed. Those bubbles with a large number of steps are always among the biggest in the field of view.

4. DISCUSSION

Bubbles in Nb-1% Zr at 1050°C grow by migration and coalescence controlled by the nucleation of critically sized ledges on their facets (Tyler & Goodhew, 1978). The same nucleation-limited mechanism has been reported for helium bubbles in Cu and Au (Willertz & Shevmon, 1970) and Al (Chen & Cost, 1974). At 1050°C facet nucleation, rather than surface diffusion, plays the major role in determining shape variations. These variations can be explained by invoking simple thermodynamic relationships whilst keeping in mind the physical processes occurring after two bubbles have coalesced.

Fig. 2. Bubbles faceted entirely on \( \{100\} \) planes after 70 h at 1050°C. Beam direction \([111]\).
S. K. Tyler and P. J. Goodhew

4.1. Bubble equilibrium conditions

A particle, or hole, at thermal equilibrium should have flat faces of low index, low energy planes, with a detailed shape governed by deep cusps in the polar surface energy $\gamma$-plot (Herring, 1953). The two minimum free energy conditions for a bubble having internal pressure $P$, strain and shape parameters $q$ and $s$ respectively, and containing $n$ vacancies at temperature $T$, are summarized as (Nelson et al., 1965):

$$P = \left( \frac{\partial}{\partial T} \int \gamma \, dA \right)_{T, s}$$

(1)

$$\left( \frac{\delta}{\delta s} \int \gamma \, dA \right)_{T, n, q=0} = 0$$

(2)

Equation (1) shows that at vacancy equilibrium the gas pressure must balance surface energy terms, while equation (2) is simply the condition of shape equilibrium, i.e. it defines the shape having the lowest total surface energy. In the absence of any anisotropy of surface energy the equilibrium shape will be a sphere, radius $r$, containing a gas pressure $P = 2\gamma / r$. A new bubble produced by coalescence of two smaller ones must come to equilibrium by absorbing vacancies, thus increasing its radius to relieve the excess gas pressure, and it must also rearrange its shape by surface diffusion. If, however, the number of vacancies available to equilibrate the

Fig. 3. A faceted bubble (B) showing well-developed steps after 25 h at 1050°C. Beam direction [111].
Irregular helium bubbles in niobium alloys

bubble is limited, and surface rearrangement is slow because of a nucleation barrier, the bubble will contain an excess pressure for a significant time at a non-equilibrium shape. This causes strain around the bubble and the minimum free energy conditions necessary to minimize the strain energy \( Q \), become (Nelson et al., 1965):

\[
\left( \frac{\partial Q}{\partial V} \right)_{T, S} = P - \left( \frac{\partial}{\partial V} \int \gamma dA \right)_{T, S}
\]

(3)

\[
\left( \frac{\delta Q}{\delta s} \right)_{T, n, q} = - \left( \frac{\delta}{\delta s} \int \gamma dA \right)_{T, n, q}
\]

(4)

Thus, as equation (3) shows, the strain energy per unit volume around the bubble is minimized for any excess gas pressure by the development of higher energy planes, thus increasing both \( \gamma \) and \( A \). It is only possible to explain the morphological changes occurring in the alloy in terms of both the atomic processes at the surfaces and the value of the vacancy flux into the bubble. These are considered in the next sections.

4.2. Bubble shape changes in Nb–1% Zr

Undoubtedly the tetrakaidodecahedra—eighteen facets comprising six square \{100\} and twelve hexagonal \{110\}—observed up to approximately 8 h represent a close approximation to the equilibrium shape. The vacancy concentration is high at short annealing times due to the extra vacancies produced during implantation. Calculations from displacement theory suggest that the upper limit to the implantation induced vacancy concentration, \( C_v \), is \( 10^2 - 10^3 \). This is low compared to those introduced by heavy ion or neutron irradiations but very high compared with the thermal equilibrium value. Many of the vacancies will be eliminated by immediate recombination but a sufficiently high concentration evidently remains to nucleate the observed density of bubbles.

Subsequently, although surface processes are nucleation controlled, surface rearrangement is possible fairly quickly because the critical step size is small for small bubbles (Tyler & Goodhew, 1978). Nelson et al. (1965) have observed the \{100\}/\{110\} tetrakaidodecahedron to be the equilibrium bubble shape in Mo.

The gradual loss of \{110\} planes and development of \{100\} planes at intermediate and longer annealing times is the result of the system following the prediction of equation (3), i.e. the development of high energy \{100\} to minimize the strain energy produced by an excess pressure. The excess pressure exists because the initial high vacancy concentration is not replenished on annealing, but is effectively reduced to the thermal equilibrium level, so the vacancy flux is insufficient for rapid size equilibration after coalescence.

The development of a cubic shape, bounded by \{100\}, seems contrary to the intuitive idea that a pressurized bubble should tend towards a spherical shape. However, a brief analysis of the energetics indicates that there may be an excellent reason for this: in the case where bubble volume must be conserved, as here, we should compare the surface energies of a sphere of radius \( r \) and a cube of identical volume. We thus find that the sphere provides a surface energy of 12.57 \( r^2 \gamma_{\text{random}} \) while the cube provides 15.59 \( r^2 \gamma_{100} \). Now if the equilibrium bubble in this material is faceted approximately equally on \{100\} and \{110\} then \( \gamma_{100} \) is likely to be 7–10% lower than \( \gamma_{\text{random}} \). This means that the cube offers the greatest surface energy to oppose the bubble pressure, unless the effect of shape on strain energy is very large. It does not seem at all improbable, therefore, that cubic bubbles should be developed in response to an excess pressure. The elongated bubbles have retained the shapes.
they acquired by coalescence because of the nucleation barrier to surface rearrangement. This is nicely illustrated by the stability of the steps shown in Fig. 3. Bubbles are larger at long annealing times and consequently have a larger critical ledge size which results in a less mobile surface.

4.3. The vacancy flow to equilibrate bubbles

To obtain some semiquantitative evidence that these bubbles do contain an excess pressure, we can consider the rate of change of bubble size by vacancy flow to the bubble using an equation similar to that originally derived by Greenwood et al. (1959) for spherical bubbles. They deduced that the rate of growth of a spherical bubble, radius \( r \), containing a pressure \( P \), in the presence of a thermal equilibrium concentration of vacancies \( C_v \) would be given by:

\[
\frac{dr}{dr} = \frac{D_v C_v \Omega}{r k T} \left( \frac{P - 2\gamma}{r} \right)
\]

where \( D_v \) is the vacancy diffusion coefficient and \( \Omega \) is the atomic volume.

If a similar derivation is used for a cubic bubble, equation (5) is only modified by the replacement of \( r \) with \( a/2 \), where \( a \) is the cube edge length.

We can now use equation (5) to estimate the time needed to relieve the excess pressure.

Rantanen & Donaldson (1970) have estimated the vacancy heat of formation in Nb to be 297 kJ mole\(^{-1}\) and hence \( C_v \) at 1050°C will be \( \sim 10^{12} \). However, if we

Fig. 4. Stronly faceted bubbles after 70 h growth at 1050°C. These large bubbles are deduced to contain an excess gas pressure. Beam direction near [001].
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consider that annealing has only reduced the concentration to $10^{-9}$ and that the vacancy diffusion coefficient $D_v$ is $\sim 10^{-19} \text{m}^2 \text{s}^{-1}$ (slightly faster than the Nb self-diffusion coefficient of $9 \times 10^{-21} \text{m}^2 \text{s}^{-1}$ at 1050°C (Smithells, 1976)), then we can estimate the shortest feasible time for a bubble to equilibrate.

Hence for $\Omega = 1.79 \times 10^{-29} \text{m}^3$, $T = 1323 \text{K}$, $\gamma_{100} \sim 1.5 \text{J m}^{-2}$ the time required for a bubble to grow from 5.0 to 5.05 nm to relieve an excess pressure of 10 MPa would be $\sim 10^{11} \text{s}$. Similarly, even if the excess pressure is 10^3 MPa the time necessary is still $\sim 10^9 \text{s}$. This clearly shows that excess pressures will exist for a long time if the vacancy concentration is near the thermal equilibrium level.

This can also be demonstrated experimentally by introducing more vacancies to a bubble population produced by long annealing times. The vacancies will be absorbed by the bubbles to initially maintain the equilibrium condition of equation (3). The flux will disturb the surface significantly, leading to faster surface rearrangement. The bubbles should become rounded initially but finally become faceted again as they equilibrate to the conditions of equations (1) and (2). We have illustrated this by reannealing the non-equilibrium bubbles produced by 70 h growth at 1050°C (Fig. 4) at 1350°C for 1 h to introduce a thermal concentration of vacancies two orders of magnitude higher. The bubbles have clearly rounded (Fig. 5) while bubbles which have been grown at 1350°C are usually faceted (Fig. 6). The bubbles must clearly contain an excess pressure.

![Fig. 5. Bubbles in the foil shown in Fig. 4 after a further anneal at 1350°C for 1 h. The bubbles have become almost spherical. Beam direction [001].](image)
4.4. The distribution of bubble sizes

It is evident from the micrographs (Figs. 1-4) that after long annealing times there is a wide distribution of bubble sizes. We have previously commented on this behaviour in the Nb-1\% Zr alloy (Tyler & Goodhew, 1978) and presented histograms showing that a small number of very large bubbles develop during annealing. Subsequent work has shown that this skew distribution of bubble size develops gradually as annealing proceeds and that the effect is much reduced in pure niobium.

The presence of large bubbles with many steps suggests that they too have grown by coalescence of smaller bubbles but the reason why a few bubbles grow more than others is not yet clearly resolved. Our experiments do not indicate that small bubbles are being channelled along dislocation lines to larger bubbles. Indeed many of the largest bubbles are not intersected by a dislocation. The rapid growth of a few bubbles is more likely to be associated with segregation of Zr to the bubble surfaces or to a strain field interaction between the corners of bubbles containing an excess pressure. In the latter case the magnitude of the effect should be related to the magnitude of the excess pressure. As the analysis of the previous section has shown, this will increase with bubble size. Bubbles which briefly become larger than their neighbours might then undergo breakaway growth as they attract the smaller more mobile bubbles to themselves. However, it is not possible at present to model the strain field of a segregant-lined, faceted brick-shaped bubble so the details of the explanation must await further work.

Fig. 6. Bubbles grown for 2 h at 1350°C showing well-developed facets due to their internal gas pressure. Beam direction [111].
5. Conclusion

Bubble shape changes occurring in Nb–1% Zr during annealing at 1050°C can be explained in terms of the competition between thermodynamic requirements and kinetics. The {100}/{110} tetrakaidodecahedra observed at short annealing times are close to the equilibrium shape because equilibration is easy due to the excess vacancies provided by the initial implantation process. The initial high vacancy concentration is not replenished by annealing but reduced to approximately the thermal equilibrium concentration. The bubbles try to adjust to new thermodynamic conditions but the nucleation barrier to surface rearrangement only allows partial fulfilment. Low energy {110} planes are lost and {100} cuboids developed—some elongated as a consequence of nucleation limited kinetics. The bubbles therefore become non-equilibrium and contain an excess gas pressure.

References