THE MOBILITY OF HELIUM BUBBLES
IN IRON AND NIOBIUM

by

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SUMMARY

The mobility of helium bubbles in iron and niobium have been measured by two different techniques. The mobility of helium bubbles in iron was investigated by applying a temperature gradient driving force to the bubbles and measurements of the migration distance were made using optical microscopy and the bubble size was estimated using the scanning electron microscope. The mobility of bubbles in niobium was investigated by measuring the rate at which the average bubble size increased with time and temperature as a result of random migration and coalescence, the measurements being taken from transmission electron micrographs.

The temperature gradient migration measurements for iron revealed that the bubbles travel up the temperature gradient, thus indicating a positive effective heat of transport. The rate of migration was compatible with a surface diffusion mechanism with a heat of transport approximately equal to the activation energy for surface self-diffusion. It is suggested that the surface transport entity is the adatom. The calculated migration rates for bubbles moving by volume diffusion or vapour transport mechanisms are considerably lower than those measured in this investigation.

The migration and coalescence results for niobium gave a log (bubble radius) versus log (time) plot with a slope of 1/5 which indicates that the bubbles move by a surface diffusion mechanism. The high values obtained for the activation energy for surface self-diffusion and the pre-exponential constant suggest that the surface transport entity is also the adatom. It has been found that the distribution of bubble sizes does not follow the simple skew distribution that would be expected from random migration and coalescence and it is suggested that interaction of bubble stress fields may be responsible.
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1. **INTRODUCTION**

The behaviour of inert gases in metals has become a technologically important subject due to the metallurgical problems found in nuclear reactors caused by the formation of inert gas fission products.

In nuclear fuels, the main problem is the swelling of the fuel element as quantities of inert gas fission products such as xenon - 133 are formed. In fuel cladding materials such as stainless steel the production of helium from boron - 10 impurities results in a serious loss in ductility due to the formation of bubbles at, and migration of bubbles to, the grain boundaries.

The fast reactor and thermonuclear reactor pose even more serious helium generation problems because the transmutation of the major constituents of the cladding material produces helium as a result of the high fast neutron fluxes found or to be expected in these environments.

Therefore the concern about dimensional stability and the strength and ductility of reactor fuel elements requires that the behaviour of inert gases in metals and oxides should be well understood, so that the consequences can be predicted in advance and the possibility of minimising these problems can be explored.

It is the purpose of this investigation to produce experimental results on inert gas bubble motion to check the validity of theoretical predictions. The experimental results that are available have not confirmed conclusively the theoretical predictions and there does not appear to be consistent agreement between different investigators.

Bubble motion studies can be divided into two categories:

(i) random migration studies

(ii) movement under the influence of an applied driving force.
This investigation consists of the former type of investigation for niobium, a prospective cladding material for the thermonuclear reactor, and the latter type of investigation for iron, the base material for the majority of fuel element cladding alloys in thermal and fast reactors.
2. LITERATURE SURVEY

The literature survey is divided into the following sections:-

2.1 The Behaviour of Inert Gas Atoms in Metals

This section reviews the available information concerning the solubility, diffusion and bubble nucleation characteristics of inert gas atoms in metals. The latter two aspects of inert gas behaviour are only included in order to get a broad understanding of the processes occurring; the primary concern here is to establish the 'insolubility' of inert gases in metals i.e. to establish that solution effects do not contribute significantly to the growth of inert gas bubbles.

2.2 The Characteristics of Inert Gas Bubbles in Metals

This section includes nucleation and growth from supersaturated inert gas solution, the size and shape of bubbles, the interaction between bubbles and the coalescence of bubbles that come into contact.

As the prime interest is the mobility of bubbles, nucleation and growth is only treated briefly in as far as is necessary to establish whether they could influence the interpretation of bubble mobility experiments. For example, if a significant fraction of bubbles are nucleated on dislocations, then the migration and coalescence characteristics upon subsequent annealing may be significantly different to that expected from homogeneous nucleation.

2.3 The Mobility of Inert Gas Bubbles

In this section the theory relating the bubble diffusion coefficient to the diffusion coefficient of the dominant diffusion mechanism is reviewed.
2.4 The Driving Forces for Bubble Migration

The driving forces which significantly affect bubble behaviour in reactor systems are reviewed. The emphasis here will be on the temperature gradient, the most important driving force both in reactor technology and mobility experiments.

2.5 The Migration Velocities of Bubbles Subjected to a Driving Force

The driving forces and mobilities are combined to give expressions for bubble velocities.

2.6 The Theory of Random Migration and Coalescence

The theory of the relationship between bubble size and annealing temperature and duration is reviewed for isothermal annealing conditions.

2.7 Review of the Experimental Results

The techniques and results of bubble migration experiments are critically reviewed and are compared with the existing theories.
2.1 The Behaviour of Inert Gases in Metals

2.1.1 The Lattice Location of the Inert Gas Atom

An inert gas atom introduced into a metal lattice may behave in any of three ways.

i) occupy an interstitial position

ii) displace a metal atom from the lattice into an interstitial position and take its place

iii) capture a thermally produced vacancy and dissolve substitutionally

Rimmer and Cottrell \(^{(1)}\) have calculated the energies of solution associated with these processes for each of the inert gases in copper, the only metal for which precise interaction potentials are available \(\text{(Huntingdon} \(^{(2)}\)). They consider the two main contributions to the energy of solution to be due to the strain energy and the loss of cohesive energy at the site of the gas atom. Using theoretical results obtained by Fumi \(^{(3)}\) they estimated the electronic contribution to the energy of formation of a vacancy and the change in electronic energy due to the dilation of the lattice around the gas atom.

Using a technique similar to that of Huntingdon \(^{(2)}\) they calculated the minimum energy configuration for an interstitial inert gas atom with respect to the neighbouring 30 copper atoms and for the simpler substitutional case the 12 nearest copper atoms were considered.

For an interstitial helium atom in copper they estimated:

\[
E_i = E \text{ (strain)} + E \text{ (electronic)}
\]

\[
= 1.7 \text{ eV} + 0.8 \text{ eV} = 2.5 \text{ eV}
\]
For a substitutional helium atom in a captured vacancy:

\[ E_{s_2} = E_{\text{strain}} + E_{\text{electronic}} + E_{\text{vacancy}} \]
\[ = 0 + 0 + 1 \text{ eV} \]
\[ = 1 \text{ eV} \]

For a substitutional helium atom in the absence of a vacancy:

\[ E_{s_1} = E_{s_2} + E_{\text{interstitial}} = 1 + 4.5 = 5.5 \text{ eV} \]

The strain and electronic energy contributions for interstitial and substitutional solution increase progressively for inert gases of increasing atomic weight.

The conclusion from these estimates of solution energies is that argon, krypton and xenon will dissolve substitutionally whether vacancies are present or not, neon will dissolve substitutionally when vacancies are present, interstitially when not, and helium will dissolve interstitially when vacancies are absent but may dissolve substitutionally when vacancies are present.

The lack of precise interaction potentials prevents the above treatment being applied to metals other than copper. Blin (4) has used compressibility data to estimate the solution energy of argon, krypton and xenon in copper, uranium and silver. The values obtained for copper are lower than those derived by Rimmer and Cottrell, but solubilities are still \( < 10^{-10} \) atomic fraction.

2.1.2 Solubility Measurements for Inert Gases in Metals

There is very little experimental information on the solubility of inert gases in solid metals. Johns (5) has measured the solubility of
argon in uranium. Solubilities were $< 3.3 \times 10^{-4}$ wt % at room temperature and $< 3 \times 10^{-3}$ wt % at 600° C, (values comparable with experimental uncertainty).

There have been many permeation experiments carried out for inert gases through metals. Permeation, in general, requires the following stages:-

i) adsorption of gas atoms on metal surface

ii) dissociation of the adsorbed molecules

iii) solution of the atoms in the metal lattice

iv) diffusion of the gas atoms through the metal

v) recombination at the exit surface

vi) desorption

ii) and v) are not relevant to inert gas permeation, but the least favourable of the remaining processes will determine the overall permeation rate. Much of the confusion in the early interpretation of inert gas behaviour in metals was due to the error in believing that lack of permeation meant that these gases did not diffuse through metals. In fact it is the lack of adsorption and the virtually zero solubility that prevents permeation, there being a finite diffusion coefficient, as first shown by LeClaire and Rowe (6) for argon diffusion in silver. Objections can often be found to experiments which have shown significant inert gas permeation through metal foils (6) (7). The exception appears to be Germanium, which is permeable to helium, though not to the other inert gases. This is presumably due to an open lattice structure and the small gas atom size (8). Several permeation experiments have been carried out for iron-helium (9) (10) (11), stainless steel-helium (12), iron-chromium-helium (13) and steel-helium (14) and in none of these investigations was there any evidence of permeation at temperatures up to 800° C.
No information appears to be available for inert gases in niobium.

The low solubility of inert gases in metals is emphasised by the lack of solubility shown by liquid metals, where the strain energy component of the heat of solution for gas solubility in solids is absent. It appears that the main contribution to the heat of solution for liquid metals is the energy necessary to make a hole in the liquid the size of the inert gas atom, the surface energy value being that obtained by extrapolation to 0K (16). The solubilities of krypton and/or xenon in a range of liquid metals (Bi, Na, Ag, Pb, Sn, In, Cd) have been reported by several authors (15) and solubilities are invariably < 10^-6 and often < 10^-10 atom fraction per atmosphere. The solubilities for helium in liquid bismuth, lithium and potassium (16) (17) do not appear to be significantly higher than for krypton and xenon. The experimentally determined solubilities for inert gases in liquid metals show a large scatter which is due to the difficulties in measuring small solubilities and the complication of surface adsorption, an error which could have been avoided by removing the surface layers before analysing the gas content (15).

2.1.3 The Diffusion of Inert Gases in Metals

a) Experimental Techniques

The diffusion behaviour of inert gases in metals have been investigated by a variety of techniques:

i) gas released (or remaining) during an isothermal anneal

ii) gas released (or remaining) during a constant rate of temperature increase (differential annealing)

iii) change of a physical property modified by the presence of the inert gas in solution (e.g. electrical resistivity or lattice parameter) during one of the above annealing treatments.
Because of the low adsorption and solubility of the inert gases, the inert gas must be introduced into the metal lattice by nuclear reactions or by ion implantation. Ions can by introduced using accelerators or by the simpler technique of using a gas discharge. This latter technique is only suitable for low ion energies (up to several tens of KV accelerating voltage), and the resulting proximity of the gas to the surface in a region where the lattice has been seriously disturbed by the bombardment is bound to complicate the interpretation of the results, as the surface condition before and during the anneal will be critically important. One technique which attempts to overcome this problem is applicable to metals that will cold weld. With this technique a 'sandwich' is formed by folding the bombarded sheet with the bombarded layer innermost and then cold rolling to give a weld. In general this technique has been troublesome and many of the results obtained by this method are in error due to leaks along microcracks in an imperfect weld, and there are also complications due to the cold-working of the material.

These difficulties are avoided by ion implantation at higher energies, where the depth of penetration is higher and surface effects are less important. Complications are introduced due to radiation damage effects, but the interaction between the inert gas and the damage is in itself an important topic.

Methods involving nuclear reactions have been used, the \( \text{(n, } \alpha \text{)} \) reactions of boron and beryllium producing helium and the fission of uranium producing xenon-133 for example.

b) Results Obtained from Gas Release Techniques

i) Gas Release During Isothermal Anneal

The fraction \( F \) of the total inert gas content released as
a function of time $t$ is measured by mass spectrometry or in the case of a radioactive isotope by activity measurement. Alternatively, the gas remaining in the sample can be measured, this being a suitable technique when a radioactive gas is used. Suitable isotopes are available for all the inert gases except helium and neon.

The simple $t^{1/2}$ dependence of gas release predicted by Fick's Law is rarely found in these experiments, due to the complication of gas precipitation into bubbles. There have been a number of 'sandwich' experiments where the ideal kinetics have been obeyed (15), but there are reasons to doubt the validity of these results due to the limitations of the 'sandwich' technique. In general, results have shown that the $t^{1/2}$ dependence is not exhibited, and that the fractional release $P$ tends to a limiting value, the rest of the gas being permanently trapped.

Because of the precipitation problem, it is necessary to analyse the initial release kinetics, before precipitation has occurred. This can be difficult, as a finite time is required to attain temperature. Also it has been found that the part of the release curve that exhibits a $\sqrt{t}$ dependence can be preceded by a region of higher release kinetics, which has been attributed variously to roughness of the surface, easy diffusion in grain boundaries, annealing of radiation induced defects, surface oxidation, evaporation, effects due to the proximity of the surface, easy diffusion along damage tracks and surface adsorption.

The only results to be considered in detail here will be those involving helium in a metal or an inert gas in iron (no results for niobium are available).

Glyde and Mayne (18) have investigated the diffusion of helium and argon in magnesium by injecting 1 MeV helium and argon ions. They found that the value for the diffusion coefficient varied with the
fraction of gas released, being initially high (particularly for argon) reducing to a minimum for $F = 0.1$ and then increasing steadily with increased gas release. The initial peak was considered to be experimental in origin, due to Rutherford scattering, which would account for the effect being more pronounced for the heavier ion (1 MeV argon). The increase in $D$ with increased gas release was considered to be due to a concentration dependence of the diffusion coefficient. They considered there to be an attraction between the argon atoms due to strain field interaction which causes the inert gas atoms to diffuse in clusters. The preferential orientation of jump directions of individual atoms towards the centre of the cluster would then reduce the diffusion coefficient by effectively reducing the value of the 'correlation factor' for the inert gas clusters. For helium it was estimated that $D$ increases by 10 as the concentration decreases by $10^3$.

They found the activation energies $Q_A > Q_{He} > Q_{self}$ as would be predicted by Swalin's (19) theory based on size differences whereas the charge difference theories of Lazarus (20) and LeClaire (21) predict $Q_A \sim Q_{He} > Q_{self}$. The activation energies are thus consistent with a vacancy mechanism where size difference determines the diffusion properties.

Glyde and Mayne also looked at the isotope effect, using argon-36, argon-40, helium-3 and helium-4. They found

\[
\frac{D_{36A}}{D_{40A}} < 1.01 \quad \text{and} \quad \frac{D_{3He}}{D_{4He}} < 1.095.
\]

deduced that the correlation factor $f < 1$, therefore ruling out interstitial diffusion but although two atom mechanisms were not eliminated by their analysis they considered diffusion by a vacancy mechanism was
indicating an inert gas-vacancy attraction.

Glyde and Mayne \textsuperscript{(22)} have also studied the diffusion of helium in aluminium. Unlike magnesium, they found that the behaviour of helium in aluminium was dominated by the precipitation of the gas into bubbles. They therefore used a low concentration of helium in their diffusion experiments (\( = 2.7 \times 10^{14} \text{ atoms cm}^{-3} \)), introduced by nuclear reaction using 150 MeV protons.

The total fractional gas release \( \gamma \) increased with decreasing concentration, \( \gamma = 0.01 \) for \( f_{\text{He}} = 10^{-3} \) atomic fraction and \( \gamma = 0.1 \) for \( f_{\text{He}} = 8 \times 10^{-9} \) atomic fraction, whereas \( \gamma = 1 \) is possible for magnesium.

Swalin's \textsuperscript{(19)} atomic size theory and LeClaire's \textsuperscript{(21)} charge difference theory both give \( Q_{\text{He}} > Q_{\text{self}} \) and the experimental results agreed with this inequality. This is not in good agreement with a previous measurement (Murray \textsuperscript{(23)}) but this was a sandwich experiment and is therefore likely to be inaccurate.

Glyde and Mayne analysed the precipitation process by looking at the departure from linearity of a \( \gamma / \sqrt{\Delta t} \) plot, which indicated that at 400\(^\circ\)C trapping occurred after approximately \( 10^{-4} \) cms and at 600\(^\circ\)C after approximately \( 3 \times 10^{-4} \) cms. The irradiation dose and temperature dependence of the trapping behaviour suggested that vacancy clusters were the trapping agents, the 'trapping ability' decreasing with increasing temperature because \( Q_{\text{self}} < Q_{\text{He}} \) and therefore the trapping efficiency becomes vacancy limited (\( \frac{D_{\text{self}}}{D_{\text{He}}} \) decreases at \( T \) increases).

The fact that helium bubbles form in aluminium, but that neither helium or argon (the latter having a large strain energy) bubbles
form in magnesium suggests that gas-vacancy interaction is not a relevant criterion for bubble formation. The stability of vacancy clusters was considered the most likely factor determining bubble formation, as quenching experiments on magnesium and aluminium have shown that visible vacancy clusters could be formed in aluminium but not in magnesium \((24)\). Glyde \((25)\) has found that noon does not permanently precipitate in silver which contrasts with copper which is known to produce inert gas bubbles (Barnes and Hazey \((26)\)), but neither metal in the pure state produce visible vacancy clusters after quenching. Therefore we have two metals with similar annealing kinetics for quenched vacancies having apparently totally different inert gas precipitation properties.

Purity is likely to be a critically important variable \((27)\) and this can complicate such comparisons.

ii) Gas Release During Differential Annealing

The main advantage of differential annealing is the way the various diffusion processes can be revealed as separate peaks on a plot of fractional release/temperature (time) when the specimen is heated at a rate typically about \(40^\circ\text{C sec}^{-1}\).

Kelly and Jech \((28)\) have described the various diffusion processes relevant to the gas release from an inert gas ion bombarded solid. They isolate the following diffusion stages:

IA  This is most prominent for low energies and low doses and occurs at temperatures well below that necessary for volume diffusion. This is caused by gas fortuitously located in high mobility sites such as interstitial sites and divacancies. Some of the gas in such sites will be released and the rest will end up in permanent traps. Another
example of a stage IA type diffusion is found in the penetrating tail phenomenon found in the range distribution of inert gas ions implanted into single crystals of tungsten \(^{(29)}\). This 'tail' is explained in terms of interstitial diffusion and it has been suggested that it may only occur in b.c.c. metals; penetrating tails have not been found in aluminium, copper or gold.

**IB** Also below the temperature for volume self-diffusion - it differs from stage IA by coinciding closely with the temperatures for the annealing of bombardment induced disorder. This stage is most prominent at high doses and is independent of the bombardment energy.

**IIA** This stage is most prominent at low doses and is due to diffusion of gas in substitutional sites in the absence of significant trapping.

**IIB** This is most prominent at moderate doses and usually appears as a satellite peak at a higher temperature than stage IIA and is explained in terms of a normal diffusion mechanism with weak trapping due to transient gas-gas or gas-damage interactions. Kornelsen and Sinha \(^{(30)}\) have found a IIB type peak in the release of neon from tungsten which they explain in terms of cluster diffusion.

**III** This is gas-release occurring at high temperatures due to bubble motion. It is most prominent at high doses.

An extensive amount of work has been carried out on the release of inert gases during differential annealing (reviewed by Carter and Colligan \(^{(31)}\), Blackburn \(^{(15)}\)). Helium appears to be the most neglected of the inert gases, but it does not seem to be significantly different in behaviour to the other inert gases. A comparison of the behaviour of
the inert gases is complicated by the different levels of irradiation damage caused by inert gas ions of different masses, and the different energies used in the various studies. Most of the investigations using ion implantation have been with the heavier inert gas ions at energies which give relatively low ranges, and the resulting gas-release behaviour is very sensitive to irradiation damage and surface effects.

Gas release measurements have been made \((32)\), helium from tungsten and helium, argon, krypton and xenon from gold, which suggest that helium does not behave significantly differently from the other inert gases except in ways which can be easily explained by damage and range differences.

No work has been reported for the diffusion of inert gases in iron or niobium, but Bauer et al \((33)\) have measured the release of xenon-133 from iron-20 wt% chromium, chosen because of the high diffusion rates in the b.c.c. iron structure, this structure being stable to the melting point for this alloy. Xenon-133 was introduced by recoil impregnation, the maximum penetration being approximately 6.5\(\mu\)m. They measured the gas release under isothermal and differential annealing conditions. In common with many other investigators, Bauer et al found that the simple \(t^{\frac{1}{2}}\) dependence of gas release was not found during an isothermal anneal, even for the lowest concentrations, but found that there was an initial burst, followed by two stages of progressively lower release rates, each stage having an approximate \(t^{\frac{1}{2}}\) dependence. Foils heated successively at three temperatures (800, 1000, 1200°C) showed these stages for each increase in temperature, but they found that the total gas release was a function of the highest temperature only and was independent of thermal route. The fraction of gas released in the initial burst and the slope of the linear portion following \(F/ t^{\frac{1}{2}}\) plot both
increased with increasing temperature, but the release rates were dependent on previous thermal history, the slope of linear portion at 800°C being much lower if the specimen had previously been heated to 1200°C. They also investigated the effect of concentration and found that the fraction released in the initial burst decreased as the concentration increased by about a factor of 10 over an implantation dose range of $2 \times 10^9 - 1.5 \times 10^{13}$ fission fragments cm$^{-2}$. The fractional release rate in the initial burst increased with decreasing concentration.

The activation energy calculated from the initial gas release is 36 k cal mole$^{-1}$, independent of concentration, a very low value compared with that for self diffusion in α-iron of 57 k cal mole$^{-1}$. The value of the diffusion coefficient decreases with increasing concentration suggesting that even initially many of the gas atoms are trapped or clustered, and that the immobile fraction increases with increasing concentration. The decrease in release rate after the initial burst is attributed to precipitation of xenon into bubbles. The decrease in the 'burst' with increasing concentration is explained by a decreased mean free path between clusters.

Bauer et al also carried out differential annealing gas release experiments and obtained release peaks at 800°C, 1100°C and 1400°C approximately. They did not state the heating rate used in these experiments, but it would appear that the first of these peaks is at too high a temperature to be explained in terms of annealing of damage, and is therefore probably the true atomic diffusion peak. The most interesting feature of the differential annealing results is the intermediate peak which they attribute to clusters or bubbles of intermediate stability. As they point out, it is necessary to introduce the concept of clusters or bubbles which are not mobile at one temperature but are at a higher
temperature in order to explain the repeated initial burst obtained each time the temperature of the specimen is increased, even though the rate of release at the previous temperature was relatively very low.

The concentration dependence of the peak values support these arguments. The first peak is most dominant for the low concentrations, as would be expected for atomic diffusion. The intermediate peak is dominant for an intermediate concentration, as would be expected for cluster diffusion and the high temperature peak is dominant at high concentrations as would be expected for bubble diffusion.

Electron microscopy of this alloy showed that the recoil implantation induced dislocations. Annealing the high dose specimens \((1.67 \times 10^{13} \text{ fission fragments cm}^{-2})\) produced bubbles, the number increasing as the annealing temperature increased.

c) **Techniques not Involving Gas Release Measurements**

Russell and Hastings \((34)\) have investigated the diffusion of helium in copper-boron alloys by following the changes in lattice parameter that occur during an anneal at a constant temperature. The copper - 0.25 at \% natural boron alloy, a single phase alloy, was irradiated to a thermal neutron dose of \(10^{19} \text{ neutrons cm}^{-2}\), producing a helium-4 concentration of 0.012 at \%. They found that the initial lattice parameter (after a 400°C stress relieving anneal) was greater than unirradiated by \(\Delta a/a = + 0.010 \%\). This was compared with theoretical predictions by Dienes \((35)\) and Huntingdon \((2)\) for copper interstitials in copper, the radius of a helium atom \((1.22\AA)\) being similar to that of a copper atom \((1.276\AA)\). Both these predicted approximately 1\% change in lattice parameter per atomic \% of interstitials, and applying simple proportionality to the helium interstitial, Russel and Hastings derived a value of
\[ \frac{\Delta a}{a} = +0.01\% \text{ for } 0.012\text{ at }\% \text{ helium, whereas substitutional solution would give } \frac{\Delta a}{a} = 0 \text{ due to the small misfit factor. It was therefore concluded that the helium was all initially in interstitial solution.} \]

Upon annealing they found that \[ \frac{\Delta a}{a} \] decreased through zero to a negative value and then increased to a positive value, the rate of change increasing with increasing temperature. The negative \[ \frac{\Delta a}{a} \] can be explained by the formation of a helium-vacancy complex, where helium enters substitutional solution associated with one or more captive vacancies. The equilibrium concentration of vacancies would not be sufficient and therefore more vacancies must be created to replace the captive vacancies. Machlup (36) has proposed that the volume increase on the formation of a vacancy in copper is less than one atomic volume, and using Machlup's estimates \[ \frac{\Delta a}{a} = -0.010\% \] would suggest between one and two vacancies for each helium atom on top of the one vacancy required to put the helium into a substitutional site (there being no significant lattice parameter change due to substitutional solution). The activation energy for this contraction process was found to be \[ 0.76 \pm 0.1 \text{ eV}. \]

The expansion from this negative value of \[ \frac{\Delta a}{a} \] back to the unirradiated lattice parameter is due to gas precipitation. The activation energy for this expansion was found to be \[ 0.96 \pm 0.1 \text{ eV}. \]

Vela and Russell (37) have investigated the behaviour of helium in copper-boron alloys by electrical resistivity measurements. These measurements are not as easily interpreted as lattice parameter measurements as there are other contributions to the resistivity changes other than gas leaving solution, such as bubble stress fields. They found that the annealing curve (resistance/log time) had two stages, the point dividing
these stages being equivalent to the point at which lattice parameter
ceases to change i.e. complete precipitation has occurred. From this they
calculated an activation energy of $0.98 \pm 0.1$ eV.

Hastings and Russell (36) have investigated the effect of concen-
tration upon the precipitation behaviour of helium in copper - 0.04 wt %
boron-10 alloy, using neutron doses sufficient to produce helium concen-
trations from 0.013 at $\%$ - 0.1 at $\%$. The change in lattice parameter was
found to be proportional to the concentration up to 0.03 at $\%$. For
higher concentrations, the helium precipitated at the irradiation tempera-
ture (75 - 100°C). Both contraction and expansion processes discussed
by Russell and Hastings (34) were found to increase linearly with increased
concentration, and the decreased precipitation time for high concentrations
would be expected to result in finer nucleation. Electron microscopy
showed this to be the case, to the extent that the bubble size was found
to increase with decreasing concentration.

Murray et al (39) have also used this technique for producing
helium i.e. the use of a boron alloying addition to produce helium by
an ($n,a$) reaction, for the study of helium diffusion in zirconium.

\textbf{d) Summary}

Despite the fact that the behaviour of inert gas atoms in
metals is not directly relevant to the study of inert gas bubble migration,
it has been reviewed here in some detail to justify the assumption made
in bubble migration experiments that an inert gas bubble migrating through
a pure metal does not lose inert gas due to the solubility of that gas
in the metal. Migration and coalescence experiments assume that bubble
growth occurs only as a result of coalescence and that there is no con-
tribution from solution effects.
The experiments reviewed in this section indicate that permanent trapping is an inevitable consequence of annealing most metal-inert gas systems. Trapping does not occur in very dilute solutions, but this is not because the trapping is not permanent, but simply because the mean free path between atomic coalescence events is large compared with the distance to the metal surface. Although most authors bring in the concept of metastable inert gas-vacancy clusters, there is no suggestion anywhere that this is anything but an intermediate temporary stage between atomic diffusion and the nucleation of stable bubbles, except in the case of magnesium and silver (18). The reported absence of bubble formation for inert gases in these two metals does not necessarily mean that bubbles, once formed, would not be stable but merely that in the experiments the right conditions for bubble nucleation did not exist. The important factor as far as bubble migration studies are concerned is bubble stability not bubble nucleation. The experimental evidence concerning the 'solubility' of inert gases in metals gives no reason to believe that resolution from bubbles should ever occur.

2.2 The Characteristics of Inert Gas Bubbles in Metals

2.2.1 Nucleation

Greenwood et al (40), have considered the nucleation of gas bubbles in uranium, and they suggested that a cluster with a binding energy of approximately 3 eV with a lifetime of approximately 100 secs would be sufficiently stable to nucleate a bubble, and they suggested that this would contain 3-6 inert gas atoms (krypton or xenon). Their theory applies to the case of continuous gas production at elevated temperature, the nucleation being determined by the balance between
nucleus stability and rate of supply of more gas atoms (which increase the stability of the nucleus).

For post-irradiation annealing, the concentration of mobile inert gas atoms is much higher and the stable nucleus size will be smaller. Hapham (41) has suggested that a cluster of 3 atoms is sufficiently stable to nucleate a gas bubble in neutron irradiated UO₂.

The nucleation sites will be a function of the condition of the material and the concentration of the inert gas. Greenwood et al (40) consider dislocations to be likely nucleation sites and Barnes and Mazey (42) consider irradiation induced vacancy clusters to be the nucleation sites. In the absence of sufficient defects for complete heterogeneous nucleation, then a certain degree of homogeneous nucleation must occur. Greenwood et al have considered the homogeneous nucleation case and have found that the result is not very sensitive to the number of atoms that constitute a stable nucleus for the case of nucleation during inert gas production. They consider that for the fission product inert gases krypton and xenon there will be a significant degree of nucleation of dislocations due to the lattice misfit, krypton and xenon having large atoms compared with uranium which would result in a strong elastic interaction (43) such that atoms are attracted to the tensile side of the dislocation forming a Cottrell atmosphere (44).

Martin (45) has considered the case of nucleation of helium bubbles in niobium. He concludes that the small size of the helium atom would result in a low strain energy for substitutional solution and that dislocations would not be a significant nucleation site. Nucleation would therefore be homogeneous.
2.2.2 Equilibrium Size of Bubbles

Once nucleated, the gas bubble will have an internal pressure which will approximately obey Van der Waal's equation, and will be balanced by the surface tension of the bubble surface and, if not in equilibrium, a strain field in the metal lattice surrounding the bubble. Elastic relaxation of the surrounding atoms can allow little volume increase for a bubble with a pressure in excess of the equilibrium value, and growth will occur by the supply of vacancies to the bubble.

When the strain field has been eliminated

\[ p = \frac{2 \gamma}{r} \]

where \( p \) is the pressure in the bubble

\( \gamma \) is the surface tension

and \( r \) is the radius of the bubble

and the Van der Waals equation can be applied to give the relationship between the pressure in the bubble and the number of inert gas atoms \( n \):

\[ \left( p + \frac{n^2 a}{r^2} \right) (\nu - nb) = nkT \]

Martin (45) has shown that the \( a \) term in Van der Waals equation can be neglected for helium, and the \( b \) term is only important for \( r < 1000 \AA \).

Therefore the number of helium atoms \( n \) in a bubble radius \( r \) is given by:

\[ n = \frac{8 \pi r^3}{3 (kT + 2\gamma b)} \]  \hspace{1cm} (1)
The number of vacancies required per gas atom increases with increasing bubble size, so that the rate of growth of the bubble is more likely to be limited by the supply of vacancies as it grows larger.

2.2.3 Bubble Growth

The rate of growth of a bubble will be determined by the rate of supply of vacancies (40) which in turn will be determined by the number of gas atoms in the bubble, although for extremely high excess pressures growth may be possible by the generation of dislocations.

Greenwood et al (40) have derived an expression for the vacancy concentration near the bubble surface:

\[ c_v = c_e \exp \left[ -\frac{(p - \frac{2 \gamma}{r}) \Omega}{kT} \right] \]  

where \( c_e \) is the equilibrium vacancy concentration and \( (p - \frac{2 \gamma}{r}) \) is the excess pressure in the bubble.

Therefore vacancies flow into the bubble to relieve the excess pressure in the bubble.

From this they calculate the rate of growth of a bubble due to vacancy absorption:

\[ \frac{dr}{dt} = \frac{D_v c_e \left( p - \frac{2 \gamma}{r} \right) \Omega}{r kT} \]

where \( r \) is the bubble radius and \( D_v \) the vacancy diffusion coefficient.
Speight (46) has analysed the bubble growth in materials supersaturated with an inert gas for the case where the diffusion of the inert gas atoms to the bubbles is rate controlling. The criterion that must be satisfied for there to be an abundant supply of vacancies is also deduced. Markworth (47) has carried out a similar analysis by a somewhat different analytical technique.

Barnes et al (48) have looked at vacancy sources in copper by observing the kinetics of bubble growth. They concluded that grain boundaries are effective vacancy sources but twin boundaries are not. They found no evidence that dislocations were significant vacancy sources.

2.2.4 Resolution

In general, the low solubility of inert gases in metals would appear to make resolution of the inert gas unlikely, except under conditions of irradiation (49). Experiments involving the migration of bubbles and the stability of bubbles on dislocations near surfaces (26) suggest that resolution does not occur.

Greenwood and Boltax (50) have analysed the possibility of gas resolution, and they conclude that resolution from small bubbles is a possible mechanism for γ-uranium which has an anomalously low activation energy for self-diffusion, but that it is is unlikely to occur generally.

2.2.5 Bubble Coalescence

If two bubbles come into contact, they will interact in two stages. The first stage, coalescence, occurs at constant volume, and the second stage, volume adjustment, involves the extra supply of vacancies necessary to re-establish equilibrium.

The treatment of this interaction in two stages implies that
the first stage proceeds far more rapidly than the second, and Nichols (51) has shown that for submicron bubbles this is a valid assumption.

The driving force for the first stage is simply the reduction in surface area resulting from coalescence, the strain energy contribution opposing coalescence (52) being less than 1% of the surface energy contribution for bubbles larger than approximately 15Å. (for $\gamma \approx 10^3$ and bulk modulus $k = 10^{12}$)

The second stage, volume adjustment to equilibrium conditions, results in a final bubble size with a surface area equal to that of the original two bubbles. Therefore

$$\Delta G_2 \text{ (surface)} = -\Delta G_1 \text{ (surface)}$$

The strain created by coalescence is relieved by vacancy supply to produce an equilibrium bubble size.

$$\Delta G_2 \text{ (strain)} = -\Delta G_1 \text{ (strain)}$$

Thus the free energy change for the entire process is

$$\Delta G_{\text{TOTAL}} = \Delta G_1 \text{ (surface)} + \Delta G_1 \text{ (strain)} - \Delta G_1 \text{ (surface)}$$
$$\quad - \Delta G_1 \text{ (strain)} + \Delta G_2 \text{ (gas)}$$
$$\quad = \Delta G_2 \text{ (gas)} < 0$$

Therefore the overall process always occurs, but as, for typical values, $\Delta G_2 \text{ (gas)} - \Delta G_2 \text{ (surface)}$ is small, and the transport mechanism (vacancy) is generally slower than surface diffusion, the second stage is much slower than the first.
2.2.6 Bubble Interaction

If bubbles are not in equilibrium but have an internal gas pressure either higher or lower than the equilibrium value, then they will have a strain field associated with them. Such strain fields have been seen in the electron microscope by Brown and Mazey (53), and the theory of strain contrast in the electron microscope has been applied to inclusions with coherency strains by Ashby and Brown (54) (55).

Brown and Mazey produced strain fields round helium bubbles in copper by rapidly cooling foils from 700°C to room temperature, thus producing bubbles with a pressure lower than the equilibrium value. The strain contrast was only visible by dark field microscopy using high order reflections as expected, low order reflections such as (111) and (200) not producing visible strain contrast. Using this technique Brown and Mazey were able to estimate the surface energy of copper, obtaining a value of 1670 ergs cm\(^{-2}\) which is in reasonable agreement with the values determined by other techniques.

If bubbles do have a strain field round them, then some interaction between the bubbles is to be expected. Such an interaction has been analysed by Eshelby (56), Willis and Bullough (57) and Liddien and Nichols (58).

In much of the literature on bubble behaviour, it has been generally assumed that the equilibrium pressure in a spherical gas bubble is given by:

\[ p = \frac{2 \gamma}{r} \]

where \( \gamma \) is the surface tension.

However, Lidiard and Nelson (59) have pointed out that the equilibrium pressure is given by :-. 
\[ p = \frac{2\sigma}{r} \]

where \( \sigma \) is the surface energy.

The strain field round the bubble, however, is zero for

\[ p = \frac{2\gamma}{r} \]

and an equilibrium bubble will therefore have a

strain field whose strength is proportional to \( (\sigma - \gamma) \), and may thus be of either sign.

Willis and Bullough have analysed the interaction between two finite gas bubbles, each of arbitrary size and with equilibrium and non-equilibrium gas pressures.

They concluded that:-

i) the interaction energy between a large equilibrium bubble (they call \( p = \frac{2\gamma}{r} \) an equilibrium bubble i.e. no strain field) and a smaller bubble under excess gas pressure is always attractive for both positive and negative excess pressures in the small bubble.

ii) the interaction increases as the distance between their surfaces decreases, becoming very large for small separations.

iii) the interaction between a large bubble and a small bubble is considerably less than the interaction between two large bubbles (excess pressures and surface separations being equal). As they only consider interaction energies, one cannot conclude that the velocity of approach is greater for the two large bubbles, as the high mobility of the small bubble will almost certainly be more significant (mobilities are discussed later in this survey).

iv) two equal bubbles with excess pressures equal in sign and magnitude and bubbles with equal excess pressures but opposite in sign
always attract each other, but the latter have the stronger attraction, particularly for small separations. For equilibrium bubbles where $\sigma + \gamma$ there is an attractive force, but Lidiard and Nelson (59) consider this force to only be significant at very close proximity, thus merely ensuring coalescence for bubbles which are virtually in contact.

Leidens and Nichols (58) have also analysed bubble interaction with other bubbles and surfaces using a computer based technique. They concluded that:

i) A gas bubble with uncompensated gas pressure will be attracted to a free surface.

ii) A gas bubble with uncompensated gas pressure will be repelled from a clamped surface.

iii) An equilibrium bubble in a linear, uniaxial or hydrostatic stress gradient will move into regions of higher stress.

iv) Their analysis for the interaction between two bubbles reaches essentially the same conclusions as Willis and Bullough.

2.2.7 Equilibrium Shape of Bubbles

The equilibrium shape of a gas bubble will depend on the variation of surface energy with orientation, and is a similar situation to that considered originally by Wulff (60) and later by Herring (61), that is, the equilibrium shape of a small single crystal particle. In general, a bubble will be faceted with flat faces of low surface energy. The shape and the sharpness of the corners will depend on the variation of surface energy with orientation, usually represented in the form of a polar plot, and the equilibrium shape is that which corresponds to the minimum surface energy.
Nelson et al. (62) have derived equations relating the internal pressure and surface energy ratios to the geometry of the bubble for bubbles with \([\{111\}, \{100\}]\) and \([\{110\},\{100\}]\) faces. They give experimental results for copper, aluminium and molybdenum. For copper they found that \{110\} planes developed preferentially in contrast to small particle annealing and grain boundary grooving experiments where \{111\} planes appeared to have the lowest energy. This suggests that surface energy values derived from these experiments may have been affected by surface contamination whereas inert gas bubbles should have clean surfaces.

For non-equilibrium bubbles Nelson et al concluded that reduced pressure in the bubble would not change the shape from that for equilibrium as the stresses produced would not be sufficient to modify surface energies. Increased pressure would cause the bubble to maximise the surface energy by becoming spherical.

2.3 The Mobility of Inert Gas Bubbles

In previous sections it has been shown that bubbles can grow by the diffusion of gas atoms and also by the coalescence of bubbles which come into contact. Bubbles can come into contact by random Brownian motion or they may be driven by some external driving force. The driving forces will be considered in a later section, and here will be regarded as an unspecified force \(F_B\) applied to the bubble.

For diffusional processes the migration velocity of a diffusing entity under the influence of an applied force \(F\) is given by

\[
V = BF
\]

where \(B\) is the mobility.
The mobility is related to the diffusion constant by:

\[ B = \frac{D}{kT} \]

So the velocity of a bubble is given by:

\[ V_B = \frac{D_B}{kT} F_B \]  \hspace{1cm} (5)

where \( D_B \) is the diffusion coefficient for the bubble.

Three basic mechanisms have been suggested for bubble diffusion - surface diffusion, volume diffusion and vapour transport.

2.3.1 Bubble Movement by Surface Diffusion

One of the earliest analyses of bubble diffusion was by Greenwood and Speight. They argued that surface diffusion would be the dominant mechanism as the activation energy for surface self-diffusion \( Q_s \) is smaller than the activation energy for volume diffusion \( (Q_f + Q_m) \) where \( Q_f \) is the energy for vacancy formation and \( Q_m \) the energy for migration.

They considered a bubble of diameter \( na \) (\( n \) atomic spacings of magnitude \( a \)). The bubble has a volume \( \frac{1}{6} \pi (na)^3 \), has \( \pi n^2 \) atoms around its surface, the jump distance is \( a \) and the jump frequency is

\[ v_D^f \exp \left( \frac{-Q_s}{kT} \right) \]

where \( v_D \) is the Debye frequency and \( f \) is an entropy factor.

The bubble is \( \frac{1}{6} \pi n^3 \) times the volume of a single atom so that the bubble jumps \( \frac{6a}{\pi n^3} \) for a single atomic jump. As there are \( \pi n^2 \) atoms on the bubble surface, the jump frequency of the bubble is
\[ \pi n^2 v_D f \exp \left( \frac{-Q_s}{kT} \right) \]

As \[ D_B = \frac{1}{6} \Gamma a^2 \]
where \( \Gamma \) is jump frequency
and \( a \) is jump distance
then \[ D_B = \frac{6}{\pi n^4} v_D f a^2 \exp \left( \frac{-Q_s}{kT} \right) \]

To compare this with equations derived elsewhere the following substitutions will be made

\[ na = 2r \]
where \( r \) is bubble radius

\[ a^3 = \Omega \]
the atomic volume

and \[ D_s = \frac{1}{4} \Gamma a^2 = \frac{a^2 v_D f}{4} \exp \left( \frac{-Q_s}{kT} \right) \]

from which:

\[ D_B = \frac{3}{2} \left( \frac{a \Omega D_s}{\pi r^4} \right) \quad (6) \]

where \( D_s \) is the diffusion coefficient for surface self-diffusion.

This is the equation derived by Nichols \(^{52}\) using a similar analysis.

Barnes and Nelson \(^{65}\) used a similar argument and assumed that \( n \) atoms migrating randomly over the surface of a bubble is equivalent to \( n^{\frac{1}{3}} \) migrating in a given direction. From this they derived:

\[ D_B = \frac{9 n^{4/3} D_s}{\pi^3 r^4} \]
For comparison, substitute \( a = \Omega \frac{1}{2} \)

Therefore

\[
D_B = \left( \frac{9}{\pi^2} \right) \frac{\Omega a D_s}{\pi r^4}
\]

Kelly (66) has derived an equation which can be transformed to equation (4), and he demonstrated that different frequency factors and jump distances can be used in these derivations provided that they form a consistent set i.e. bubble jumps or surface jumps can be considered.

Shewman (67) and Gruber (68) have approached bubble migration due to surface diffusion by considering there to be a force \( f_a \) acting on the individual atoms, the former analysis being in terms of bubble movement, the latter in terms of surface movement. Shewman's equation derived by considering the surface flux across the circumference of a bubble is:

\[
\frac{dx}{dt} = -\left( \frac{2D_s \delta}{kTr} \right) f_a
\]

where \( \delta \) is the thickness of the high diffusivity surface layer.

To compare this with previous derivations, the relationship between the force on an atom and the force on the bubble must be obtained. If \( F_b \) is the equivalent force on the bubble, and the bubble is moved a distance \( \ell \) then the work done is \( F_b \ell \) which is equivalent to the work done by the force \( f_a \) on moving

\[
\left( \frac{4 \pi r^3}{3 \Omega} \right) \text{ atoms a distance } \ell \text{ in the opposite direction.}
\]

Therefore:

\[
f_a = -\left( \frac{3 \Omega}{4 \pi r^3} \right) F_b
\]
Substituting \( v = \frac{dx}{dt} \), \( \delta = a \) (an assumption) into equation (7) and using equations (5) and (8), equation (6) is obtained exactly.

Gruber's (68) calculations are somewhat more rigorous, and make no assumptions about the shape of the bubble during migration (although he does consider the bubble to be initially spherical). Like Shewmon, he considers there to be a force \( f_a \) on the individual atoms, but he calculates the movement of a bubble surface element in a direction normal to the surface due to the surface flux:

\[
\frac{dp}{dt} = -\frac{\Omega \nu D_s f_a}{\pi r^4} \cdot \cos \theta \tag{9}
\]

where \( \nu \) is the surface density of atoms involved in surface diffusion.

If equation (8) is substituted into this and, the translational velocity found by putting \( \theta = 0 \), then:-

\[
V = \frac{3 \nu D_s}{2 kT \pi r^4} \cdot F_b
\]

From equation (5)

\[
D_B = \frac{3}{2} \frac{\Omega \nu D_s}{\pi r^4} = \frac{3}{2} \frac{a^4 D_s}{\pi r^4}
\]

Gruber did not state the equations in this form but substituted

\[
\Omega \nu = \Omega^{1/3} = 0.891 \ a \text{ for the f.c.c. lattice where}
\]

\( a_0 \) is the interatomic distance where

\[
\Omega = \frac{a^3}{\sqrt{2}} \text{ to give}
\]

\[
D_B = 0.301 D_s \left( \frac{a}{r} \right)^4
\]

and

\[
\nu = -\left( \frac{1.78 a D_s}{\pi r^4 kT} \right) f_a
\]
He noted the close agreement with the analyses of Greenwood and Speight (64) and Shewmon (67) but failed to point out that the differences were not due to his analytical technique, but to the substitutions made: \( \Omega v = 0.891 a \) and \( \Omega = \frac{a^3}{\sqrt{2}} \) instead of \( \Omega v = a \) and \( \Omega = a^3 \) as used in most other analyses. The latter substitutions give equation (6) exactly.

It is interesting to note that equation (9) i.e. \( \frac{dp}{dt} = \text{const} \times \cos \theta \) means that the bubble remains spherical during migration.

In general, it would seem that the main doubts concerning the surface diffusion mechanism concerns the exact nature of the surface diffusion i.e. the surface concentration of diffusing atoms and the jump distance. This will be further considered in a later section.

The analysis of bubble motion can therefore be carried out two ways, one the bubble mobility approach the other by an atomic mobility approach.

The bubble mobility technique has the advantage of simplicity, but the validity of this approach is not obvious. The atomic mobility approach is more fundamental and can be used to show that a spherical bubble remains spherical during migration, a fact which is assumed and not proven in the bubble mobility technique.

2.3.2 **Bubble Movement by Volume Diffusion**

The bubble diffusion coefficient for volume diffusion has been evaluated by a similar technique to that used for surface diffusion. Nichols (52), Barnes and Nelson (65) and Kelly (66) have presented similar analyses using bubble mobility and Shewmon (67) in terms of atomic mobility.
From Nichols (52),

\[ D_b = \frac{1}{6} \Gamma_b \lambda_b^2 \]

where \( \Gamma_b \) is jump frequency of bubble
\( \lambda_b \) is jump distance

\[ \Gamma_p = \Gamma_v \left( \frac{4/3\pi r^3}{\Omega} \right) \]

\[ \Gamma_v = \frac{6D_v}{\lambda^2} \]
\[ \lambda_p = \lambda \left( \frac{3\Omega}{4\pi r^3} \right) \]

where \( \Gamma_v \) is atomic jump frequency (for volume diffusion)
\( \lambda \) is atomic jump distance

Combining these equations:

\[ D_b = \frac{3}{4} \left( \frac{D_v \Omega}{\pi r^3} \right) \]  \( (10) \)

where \( D_v = \frac{D^*}{f} \)

\( D_v \) - volume diffusion coefficient
\( D^* \) - tracer diffusivity
\( f \) - correlation factor

Barnes and Nelson (65) give a similar equation with a numerical constant of unity.

Kelly's (66) analysis is rather more complicated, involving several extraneous parameters which eventually cancel out, leading to a similar expression with a numerical constant of \( \frac{3}{2f} \), where \( f \) is a correlation factor.

Shewmon (67) presents an analysis using atomic mobilities, and he uses an analogy with electrostatic potential theory to obtain a similar
result with a constant of \( \frac{1}{f} \), where \( f \) is a correlation factor.

It is interesting to note that if \( r = a \) (atomic radius) is substituted in equation (10) then:

\[
D_B = D_v
\]

2.3.3 **Bubble Movement by Vapour Transport**

The equations for vapour transport have been derived in a similar manner.

Nichols \( (52) \):

\[
D_B = \frac{3 D_g \Omega^2 a_v P_v}{4 \pi kT r^3}
\]  

where \( a_v \) \((\ll 1)\) measures departure from equilibrium

\( P_v \) is the equilibrium vapour pressure

Substituting \( v_g = \frac{a_v P_v}{kT} \)

and \( v_s = \Omega^{-1} \)

\[
D_B = \frac{3 \Omega D_g}{4 \pi r^3} \left( \frac{v_g}{v_s} \right)
\]

where \( v_g, v_s \) are the atomic densities of vapour and solid respectively.

Barnes and Nelson \( (65) \):

\[
D_B = \frac{\Omega^2 D_g P_T}{2 \pi r^3 kT}
\]
Substituting \( \nu_g = \frac{P_T}{kT} \)

\( \nu_s = \Omega^{-1} \)

\[ D_B = \frac{1}{r^2} \frac{\Omega D g}{\pi r^3} \left( \frac{\nu_g}{\nu_s} \right) \]

They point out that as

\[ D_g = \frac{kT \nu}{6\sqrt{T} \pi r^2 P} \]

where \( \nu \) is the average velocity of the diffusing atoms through the gas

and \( p \) is the cross-sectional radius for collisions between vapour and gas atoms

and \( P \) is the gas pressure \( (= \frac{2 \gamma}{r}) \)

then \( D_B \propto 1/r^2 \) for a gas bubble

but \( D_B \propto 1/r^3 \) for a void

whereas the surface and volume diffusion mechanisms would be unaffected by the gas pressure.

Kelly \((66)\) uses a rather complicated analysis and ends up with an equation which is dimensionally incorrect.

Shewman \((67)\) uses an atomic mobility approach to derive:

\[ \frac{dx}{dt} = -\frac{D g}{kT} \left( \frac{\nu_g}{\nu_s} \right) \cdot f_a \]

He suggests that

\[ f_a = \frac{-\Omega}{2 \pi r^3} \cdot \frac{p_b}{p} \]
(rather than \( \frac{3}{4} \pi r^3 \) more commonly used)

Therefore

\[
D_B = \frac{1}{2} \frac{D_g G}{\pi r^3} \left( \frac{\nu g}{\nu s} \right)
\]

Speight (69) has analysed vapour transport for the specific case of a temperature gradient and obtained:

\[
V = \frac{D_g}{kT} \left( \frac{\nu g}{\nu s} \right) \left( \frac{L}{T} \right) \frac{dT}{dx}
\]

where \( L \) is the latent heat per atom.

Assuming that:

\[
f_a = \frac{L}{T} \left( \frac{dT}{dx} \right)
\]

(this will be discussed in a later section) then this equation is identical to equation (11).

2.3.4 Summary of Diffusion Controlled Bubble Movement Mechanisms

The surface diffusion mechanism has been given more attention by various investigators than the other two mechanisms, as it is generally believed to be the dominant mechanism for small bubbles in metals. The relative importance of these mechanisms will be discussed in a later section when the various driving forces have been considered.

Summarising:

\[
D_B = \frac{D_S}{r^4} \quad \text{(surface diffusion)}
\]

\[
D_B = \frac{D_V}{r^3} \quad \text{(volume diffusion)}
\]
\[ D_B = \frac{D_0}{r^3} \propto \frac{1}{r^2} \] (vapour transport in gas filled bubble)

\[ \propto \frac{1}{r^3} \] (vapour transport in void)

The radius dependence will favour the surface diffusion mechanism for small bubbles, vapour transport for large bubbles. In general, \( Q_s < Q_v < \Delta H_v \), so that surface diffusion will be favoured at low temperatures and volume or vapour transport at higher temperatures.

2.3.5 Interface Controlled Mobility

The previous sections have reviewed the analysis of bubble mobility starting from the assumption that the mobility is diffusion controlled. Shewmon (67) has pointed out that there is a distinct possibility that the migration of bubbles may be interface reaction controlled. Shewmon's treatment of this was rather general and more relevant to a particle than a bubble.

Willertz and Willertz and Shewmon (71) have shown diffusion rate-controlling mechanisms to be inappropriate when applied to faceted bubbles in copper and gold. They used the Terrace-Ledge-Kink surface diffusion model (72) (73) (74), to illustrate how the nucleation of fresh atomic layers in a faceted bubble could explain the low mobilities they found for inert gas filled bubbles in copper and gold foils.

Most of the published work has considered the effect of interface control as a limitation to the rate of surface diffusion. Choi and Shewmon (75) and Gjoestein (73) have analysed the energy differences atoms experience in moving from one type of surface site to another.

Figure (1) shows the various types of position that a surface atom can
occupy, each position characterised by a co-ordination number which can vary from \( n = 3 \), a surface adatom to \( n = 9 \), a terrace position. In general, a surface flux can be carried by either of two intrinsic defects, the adatom or the terrace vacancy.

Assuming, say, adatom diffusion to be the dominant mechanism for surface diffusion, then the activation energy for surface diffusion will be \( \Delta H_{3m3} \) where \( 3m3 \) denotes the energy barrier for the diffusion jump from one adatom position \( (n = 3) \) to another. But if the surface is atomically 'clean', with no adatoms available, the activation energy for surface diffusion will have to include a term for the formation of an adatom (and a terrace vacancy) from a terrace position. Gjostein (73) has derived an expression:–

\[
D_s = \frac{2}{4} \sum_{i=1}^{p} \left\{ \sum_{j=1}^{N} \frac{n_i}{n} \right\} \beta_{ij} \nu_{ij} \exp\left[ \frac{-\Delta G_{imj}}{RT} \right]
\]

where

- \( \Delta G_{imj} \) is the difference in free energy between the \( i^{th} \) site (equilibrium position) and the saddle point between the \( i^{th} \) and \( j^{th} \) site.
- \( \nu_{ij} \) is vibrational frequency about the \( i^{th} \) site in the direction of the \( j^{th} \) site.
- \( \beta_{ij} \) is the number of nearest neighbouring sites of the \( j^{th} \) type.
- \( N \) is the number of classes of sites that have distinguishably different values for the index \( j \).
- \( \frac{n_i}{n} \) is the fraction of surface atoms occupying \( i^{th} \) sites at any instant.
Applying this equation to adatom formation and migration

\[ \beta_{3j} = 3, \ \beta_{9j} = 6, \ \nu_{ij} = v \]

Then:

\[ D_s = \frac{3 \xi^2 v n_9}{4 n} \left\{ \frac{n_3}{n_9} \exp\left[\frac{-\Delta G_{3m3}}{RT}\right] + 2 \exp\left[\frac{-\Delta G_{9m3}}{RT}\right] \right\} \]

At equilibrium,

\[ \frac{a_3 a_v}{a_9} = \frac{(\frac{1}{2} \frac{n_3}{n_9})^3}{(\frac{1}{2} \frac{n_3}{n_9})^3} = \exp\left[\left(\frac{-\nu_3^o + \nu_v^o - \nu_9^o}{RT}\right) \right] = \exp\left[\frac{-\Delta G_{39}^o}{RT}\right] \]

where \( a_i \) is the activity of atoms in the \( i \)th site (\( v \) - vacant site)

Therefore

\[ \frac{n_3}{n_9} = \sqrt{2} \exp\left[\left(\frac{-\frac{1}{2} \Delta G_{39}^o}{RT}\right) \right] \]

Therefore

\[ D_s = D_o \exp\left[\frac{-Q_s}{RT}\right] \]

where

\[ D_o = \frac{3\sqrt{2} \xi^2 v}{4} \exp\left[\left(\frac{1}{2} \Delta S_{39}^o + \Delta S_{3m3} \right) / R \right] \]

and

\[ Q_s = \frac{1}{2} \Delta H_{39}^o + \Delta H_{3m3} \]

Therefore, when surface self-diffusion takes place in a situation where adatoms are not readily available, as in a faceted bubble, then the activation energy:

\[ Q_s = \frac{1}{2} \Delta H_{39}^o + \Delta H_{3m3} \]

(12)

not merely \( Q_s = \Delta H_{3m3} \)
Gjostein estimates
\[ \Delta H_{3m3} < \frac{\Delta H_s}{6} \]

where \( \Delta H_s \) is the heat of sublimation

Willertz (70) estimates
\[ Q_s = \frac{1}{2} \Delta H_{39}^0 + \Delta H_{3m3} \approx \frac{3}{5} \Delta H_s \]

i.e. \( Q_s \approx \Delta H_{3m3} \)

The above treatment is valid if the bubble facets are crystallographically perfect and adatoms have to be nucleated out of the terraces (terrace-ledge-kink model terminology). If ledges are available the activation energy will be lowered. Values have been estimated by Choi and Shewmon (75) and Gjostein (73). Both analyses suggest that the activation energy in this case will still be significantly higher than \( \Delta H_{3m3} \).

Willertz (70) proposes a simple model for faceted bubble migration. Atoms move from in-surface positions to adatom positions on one face, the vacancies formed then coalesce to minimise the total edge energy thus forming a 'pillbox' shaped depression and the adatoms coalesce to a 'pillbox' of atoms on another facet. The bubble therefore moves a single atomic distance and then remains stationary until another 'pillbox' is nucleated. Using this model Willertz and Shewmon (71) have derived a bubble diffusion coefficient. The expression obtained is of the form:

\[ D_b = \alpha r \exp \left( -\beta r \right) \]  

This is an effective bubble diffusion coefficient, averaging the intermittent motion of the bubbles.
An equation of this type is probably a reasonable explanation for reduced mobility in faceted bubbles, but it is noticeable that Willertz (70) makes no attempt to fit his data to this equation.

Beere (76) has attempted to use this equation to explain the results of Cornell and Bannister (77), Walker (78) and Gulden (79).

He concluded that the ion implantation technique used by Cornell and Bannister (77) and Walker (78) led to a significant fraction of the bubbles being precipitated on dislocations (80) and therefore are not migrating randomly.

The bubbles observed by Gulden (79) however, were created during bulk neutron irradiation of uranium dioxide pellets and were not attached to dislocations. A plot of $\log_{10} \frac{D_b}{r}$ versus $r$ showed a reasonable correlation with equation (13), except that the value of the pre-exponential constant was in disagreement with Willertz and Shewmon's (71) derivation by many orders of magnitude. Beere derives an alternative pre-exponential constant which gives reasonable agreement with Gulden's results. Beere also analyses the case of temperature gradient migration, $10^6 \text{ cm}^{-1}$ at $2000^\circ \text{ K}$, for uranium dioxide and concludes that migration will be nucleation limited.

Beere (80) has analysed the random motion of faceted bubbles along dislocations. His analysis provides an explanation for his own results and those of Cornell and Bannister (77) and Walker (78). Beere (80) shows that dislocations introduce steps into the bubble surface and reduce the critical nucleation energy compared with bubbles not intersected by dislocations. Thus bubbles intersected by a dislocation are more mobile than bubbles in a perfect lattice, but their motion is directed along the dislocation.

Beere and Reynolds (81) have investigated and analysed the
effect of interface control on the growth and contraction of gas bubbles due to the application of alternately high and low external pressures. They found that bubbles did not change in size uniformly and did not achieve equilibrium shapes. Asymmetric growth of bubbles on dislocations suggested that the rate of approach to equilibrium was interface controlled, vacancy absorption being favoured on the faces intersecting the dislocation. They concluded that bubbles deviating only slightly from equilibrium shape have small driving forces for atomic transfer between faces and that the rate of approach to an equilibrium shape is very slow and nucleation rate controlled.

Bubble migration with a significant driving force may alter the relative importance of interface control and diffusion in determining bubble mobility. Cahn (82) has suggested that above a certain driving force even a singular interface can move without the need for nucleation.

The driving force which has received the most attention is the temperature gradient. De Crescenz and Selleck (83) found that helium bubble migration in uranium carbide was surface diffusion controlled. Oldfield and Brown (84) concluded that migration in uranium dioxide was interface controlled. Buescher and Meyer (85) concluded that the temperature gradient induced migration of bubbles in uranium dioxide was vapour transport controlled for \( r > 1\mu\text{m} \), intermediate sizes surface-gas mechanism controlled and small sizes \( r < 100\text{Å} \) interface controlled.

The temperature gradient work will be discussed in greater detail later, but it is interesting that the Buescher and Meyer (85) analysis introduces another diffusion mechanism for bubble mobility. It is suggested that surface diffusion jump distances in uranium dioxide at the temperatures considered is in the regime described by Gjostein (86) and Bonzel (87) as nonlocalised migration. This is a
process involving large adatom jumps i.e. the atoms 'skate' across the surface. Under these conditions it is suggested that the gas atoms in the bubble limit the migration distance across the surface to approximately the mean free path of the gas in the bubble. From this they predict that the migration rate of the bubble would be independent of radius.

The weakness of this theory would appear to be the assumption that collision with a gas atom will stop the migrating adatom whereas its effect is more likely to be an increased randomisation of the biased migration of the surface adatoms.

2.3.6 Other Variables Affecting Bubble Mobility

a) Surface Diffusion Characteristics

i) F.C.C. Metals

Gjostein (88) has suggested that two surface diffusion mechanisms are operative in f.c.c metals. The high temperature mechanism ( for \( l > T/T_m > 0.77 \), where \( T \) is the temperature and \( T_m \) the melting point in °K), is characterised by a high value for \( D_o \), the pre-exponential constant (approximately 740 cm\(^2\) sec\(^{-1}\)) and a high activation energy (approximately 30 Tm cal mole\(^{-1}\)). The low temperature mechanism ( \( T/T_m < 0.77 \) ) is characterised by a low value for \( D_o \) (approximately \( 1.4 \times 10^{-2} \) cm\(^2\) sec\(^{-1}\)) and a low activation energy (approximately 13 Tm cal mole\(^{-1}\)). The resultant temperature dependence of surface self-diffusion is given in Figure (2).

The high temperature mechanism is explained in terms of adatom diffusion. The high activation energy, as mentioned previously, is due to the high value for \( \Delta H_f^a \) (heat of formation of an adatom) whereas \( \Delta H_m^a \) (migration) is almost certainly very low. The large value of
$D_0$ has been explained by Hirth (89) in terms of a marked dependence of vibrational frequencies of surface atoms as a function of their particular surface position. Alternatively Shewmon and Choi (90) and Gjostein (88) have suggested that the adatom in its activated state translates freely over the surface and Gjostein estimates that jump distances of about 5 atomic spacings occur. Measurements of adatom diffusion using the field ion microscope technique confirm that the activation energy for adatom migration is extremely low:

\[ \text{e.g. } Q_m \text{ for a tungsten adatom on a (211) tungsten surface is only } 13 \text{ k cal/mole.} \]

The low temperature mechanism is considered by Gjostein (88) to be due to a surface vacancy mechanism. The calculation of $\Delta H^s_F$ for a surface vacancy encounters all the difficulties of the equivalent calculation for a bulk vacancy i.e. the highly significant electron redistribution contribution to the formation energetics. The relaxation around a surface vacancy should not be as inhibited as in the bulk. This relaxation should also reduce the saddle position energy compared with the bulk case.

The value of $D_0$ for surface diffusion in this low temperature regime is therefore lower than that for bulk vacancy diffusion.

Matsumura (91) has obtained values of $Q_s = 53 \text{ k cal mole}^{-1}$ (29Tm) and $D_0 = 5.2 \times 10^2 \text{ cm}^2 \text{ sec}^{-1}$ for $\gamma$ - Fe using a wire sintering technique. Blakely and Kykura (92) used grain boundary groove and scratch techniques and obtained a similar value for $Q_s$ but found $D_0 = 4 \times 10^3 \text{ cm}^2 \text{ sec}^{-1}$. It would appear from these results that the high temperature mechanism is operative in $\gamma$ - Fe.
ii) B.C.C Metals

A plot of \( \log_{10} D_s \) vs \( Tm/T \) for the b.c.c metals (see Figure 3) reveals two important points:

i) the plot for each metal is linear, suggesting that only one mechanism is operative

ii) different b.c.c metals behave differently and are very sensitive to impurities.

An average curve for b.c.c. metals would give:–

\[
D_s = 3.6 \exp \left[ \frac{19 Tm}{RT} \right] \tag{14}
\]

The values for \( D_0 \) and \( Q_s \) are both intermediate between the values for the two mechanisms in f.c.c metals.

The fact that the plot is linear down to relatively low \( T/Tm \) values suggests that the low temperature mechanism (i.e. surface vacancies) is operative, although the values of \( D_0 \) and \( Q_s \) make this conclusion somewhat speculative. The greatest doubts are for the mechanism operative in \( \alpha \)-Fe. Zahn (93) has measured the surface diffusion constants for \( \alpha \)-Fe using a sinusoidal profile decay technique in a hydrogen atmosphere and obtained \( Q_s = 59.6 \text{ k cal mole}^{-1} \) (35 Tm) and \( D_0 = 5 \times 10^5 \text{ cm}^2 \text{ sec}^{-1} \). Matsumura (91) obtained \( Q_s = 58 \text{ k cal mole}^{-1} \) and \( D_0 = 2.4 \times 10^4 \text{ cm}^2 \text{ sec}^{-1} \) using a wire sintering technique. Blakely and Mykura (92) obtained a similar activation energy to Matsumura using grain boundary groove and scratch methods but found \( D_0 = 10^5 \text{ cm}^2 \text{ sec}^{-1} \). These results would suggest an adatom mechanism.

Some interesting work on adatom surface mobility in b.c.c tungsten has been carried out by Zährlich and Kirk (94) in the field ion microscope which shows that the surface diffusion characteristics can be
very different on different crystallographic planes. The (211) surface plane in particular shows a tendency toward directed motion along the closely packed [111] direction and a particularly low value of $D_o$ for diffusion on this plane.

iii) Impurity Effects

Gjostein (88) has reviewed the effect of impurities on the surface diffusion properties of metals.

It is evident that the major cause of the large scatter in surface diffusion results is due to unintentional contamination of the surface; the early work of Blakely and Nykura (95) (96), on nickel and platinum in a poor oil pumped vacuum being a good example, their results giving low values for $D_s$ and a marked orientation dependence.

Certain adsorbed impurities such as oxygen and sulphur are known to increase $D_s$ for silver and copper (97) (98) (99).

Low energy electron diffraction studies on silver, gold, platinum and palladium have revealed surface repeat distances of several times the normal which Fedak and Gjostein (100) (101) attribute to impurity effects.

With a property such as surface diffusion where the active mobile entity on the surface (adatom or surface vacancy) occupy only a small fraction of the available surface, it is to be expected that such a property would be very sensitive to impurities. This would be particularly true for a surface vacancy which might be expected to minimise surface energy by forming impurity vacancy complexes. The mobility of such a complex may be smaller or larger than a surface vacancy depending on the jump frequency of the particular impurity atom.
In contrast an adatom does not have the distortion field surrounding it with which it could interact with an impurity atom, thus producing a smaller binding energy for an adatom impurity complex.

This is in agreement with the experimentally observed fact that impurity effects are most pronounced at low temperatures in f.c.c and in b.c.c metals i.e. where the surface vacancy mechanism is operative, and that impurities can produce increases or decreases in the value of $\Delta_s$.

Gjostein (73) (102) has also suggested that the pinning of ledges by impurities will result in a decrease in the value of $\Delta_s$.

b) Surface Energy

Surface energy is an important variable to consider because it affects the tendency towards faceting (due to anisotropy of surface energy) and, like surface diffusion, is affected by very small impurity levels.

For example, Clarebrough et al (103) observed faceted vacancy clusters in copper and found {111} and {100} type planes present on facets in foils annealed in a reducing atmosphere, whereas in addition the {110} planes were also faceted in foils annealed in vacuum or argon. This reduction in surface energy anisotropy, due presumably to oxygen, would result in rounder bubbles with more faces and more ledges from which adatoms could nucleate, thus reducing the tendency toward interface limited migration.

The theory of surface energy and its anisotropy has been reviewed by many authors including Mullins (104), Ehrlich (105) and Winterbottom (106) and the effect of impurities and alloying elements by Hondros and McLean (107). McLean (108) has measured the surface
energy of copper as a function of crystallographic orientation and temperature. He found that the anisotropy of surface energy decreased with increasing temperature. Hondros' has measured the surface energy of δ-Fe as a function of the oxygen content of the ambient atmosphere using a zero-creep technique and found a decrease in surface energy with increasing oxygen partial pressure.

c) Precipitates

Although the subject being reviewed is the mobility of inert gas bubbles in pure metals, it is important to remember that very small quantities of certain contaminants may produce fine precipitation which for example could appear as 'spots' on a high resolution electron micrograph. Some of the copper foils used by Willertz' had such precipitation which he suggested may be caused by decomposed vacuum pump oil. This is a particular danger when foils are prepared by vapour deposition in anything other than ultra-high vacuum systems. Such precipitates could greatly influence the migration characteristics of inert gas bubbles.

The reduction in surface energy caused by coalescence with a precipitate particle will give rise to a strong binding force. Barnes and Nelson' estimate that with a typical precipitate interfacial energy of 300 dyne cm$^{-1}$ and a temperature gradient of $10^3$ °C cm$^{-1}$, bubbles of up to 4500° will remain adhered to the precipitate. This estimate is for a precipitate of a similar size to the bubble or greater; the binding force for a 'spot' type precipitate in an electron micrograph will be lower, but still significant, particularly in random migration studies.
d) **Dislocations**

Beere \((80)\) has discussed the interaction between a bubble and a dislocation from the point of view of bubble interface kinetics and bubble mobility along the dislocation.

Weeks et al \((110)\) have analysed the elastic interaction between a dislocation and a bubble or particle. They divide this interaction into two components, a long-range and a short-range interaction.

a) **Long range interaction**

Using the result of Eshelby \((111)\) for the interaction energy of a particle with a uniform applied stress field in conjunction with Cottrell's \((44)\) expression for the stress field of a screw or edge dislocation, they derive the following interaction energies for bubbles with dislocations:

\[
\begin{align*}
E_{\text{SCREW}} & = \frac{-5G b^2 a^3}{2\pi} \frac{(1-v)}{(7-5v)} \cdot \frac{1}{r^2} \\
E_{\text{EDGE}} & = \frac{-5G b^2 a^3}{2\pi} \cdot \frac{1}{(7-5v)(1-v)} \cdot \frac{1}{r^2} \\
& \quad \{ 1 - \frac{(1+6v-5v^2)}{5} \sin^2 \theta \}
\end{align*}
\]

where \(G\) is shear modulus,

\(a\) bubble radius

\(r\) distance between bubble and dislocation,

\(b\) the Burgers vector

\(v\) Poisson's ratio

and \(\theta\) the angle between the Burgers vector and \((r,\theta)\)

are the cylindrical co-ordinates of the bubble relative to the dislocation.
These expressions are approximate as Eshelby's result only strictly applies to a uniform stress field and should only be used for (say) $r > 5a$

b) Short-range interaction

Crude estimates of the interaction energy of a bubble that lies symmetrically on a dislocation line have been made by Barnes (112), Cahn (113) and Weeks et al (110), by calculating the elastic energy originally stored in the volume now occupied by the bubble. The latter is the most refined estimate:

$$E_{\text{MAX}} = -\frac{G b^2 a}{2\pi} \left( \ln \frac{2a}{r_o} - 1 \right)$$

where $r_o$ is the inner cut off radius used in the standard calculation of the elastic energy of a dislocation.

A rigorous analysis by Weeks et al (110) allowing for the elastic relaxation at the bubble surface gives

$$E_{\text{MAX}} = -\frac{G b^2 a}{2\pi} \left( \frac{2}{12} + \ln \frac{a}{r_o} \right)$$

$E_{\text{MAX}}$ is always negative, meaning that the interaction is an attractive one, and the rigorous analysis gives a value which is typically 25\% higher than that calculated from the simple estimate.

The significance of the long-range interaction is that under conditions of random migration (in the absence of external directed driving forces) there can be a significant force attracting bubbles towards dislocations ($E_{\text{INT}}$ for a bubble is always negative i.e. attractive). Weeks et al (110) estimate that all 10000 bubbles within a 100000\$ radius of
a screw dislocation will be attracted onto the dislocation within $10^4$ seconds, assuming a temperature of $10^3$ °K, $D_s = 10^{-8}$ cm$^2$ sec$^{-1}$ and $G = 4 \times 10^{11}$ dynes cm$^{-2}$.

The short range interaction has been estimated by Weeks and Scattergood (114) to be so strong that in the case of UO$_2$ that the force on the bubble necessary for breakaway of bubble from a dislocation is determined, not by the interaction force, but by the line tension of the dislocation i.e. the dislocation will bow out into a dipole configuration before bubble release. Forty (115) has observed dislocations trailing behind migrating bubbles in lead iodide crystals and Weeks, Scattergood and Pati (116) have extended this concept to uranium oxide and carbide and have analysed the reduced mobility caused by a trailing dipole of dislocation (or grain boundary). They show that the continued interaction caused by such a trailing dipole significantly reduces the migration velocities of bubbles with less than about twice the critical radius for release from the dislocation.

e) Grain Boundaries

In a similar manner to the dislocation case discussed in the previous section, grain boundaries can sweep bubbles along with them and bubbles can restrain the movement of grain boundaries. This will not be reviewed here as the interaction with grain boundaries is not important in bubble mobility studies as, unlike dislocations, the interaction can easily be avoided by looking at areas well clear of the grain boundaries or by using single crystals.
The most significant driving forces for bubble migration in metals are:

1) Stress gradients
2) Bowed dislocations
3) Moving grain boundaries
4) Temperature gradients

The experimental work carried out for this thesis was directed towards bubble behaviour with the latter of these driving forces or with no driving force at all i.e. random migration. This latter case will be reviewed in a subsequent section.

2.4.1 Stress Gradients

Some attention has been given to stress gradients as a driving force because of the technological interest in bubble migration in nuclear fuels. Martin (117), Willis and Bullough (57) and Leiden and Nichols (58) have analysed the interaction of a bubble with a stress field. The latter two papers have summarised the conclusions relevant to the work of this thesis i.e. the effect of the stress fields round a bubble on bubble-bubble interaction and this has been reviewed in a previous section (Bubble Interaction). The experimental conditions for random migration and temperature gradient studies do not in general give rise to stress gradients.

Martin (117) has analysed the interaction of an equilibrium bubble with a stress gradient, and this leads to different conclusions compared with the other analyses which assume that the bubble has a
constant size. An equilibrium bubble will change in size by vacancy absorption (assuming that the concentration of vacancies is sufficient to allow equilibrium to be maintained) as it moves in the stress gradient. Martin finds that the contribution to the interaction with the stress gradient from the change in volume of the gas in the bubble and the change in surface area of the bubble dominate and that matrix strain energy contribution is insignificant except perhaps for extremely small bubbles \((r < 10^{\text{6}})\), and the matrix strain energy contribution is always opposite in sign to the volume/surface area contribution. Consequently equilibrium bubbles migrate to regions of lower stress but constant volume bubbles migrate to regions of higher stress.

2.4.2 Bowed Dislocation

This has been reviewed in a previous section as a restraint to bubble movement. In a system where dislocations are moving they can provide a driving force.

In random migration studies it is the restraining effect of dislocations which is significant whereas in temperature gradient dislocation climb due to the vacancy flow could conceivably cause a migration driving force.

2.4.3 Moving Grain Boundaries

This situation could arise in temperature gradient experiments if there is a tendency for grain boundaries to move as a result of the temperature gradient \((118)(119)(120)(121)(122)\) forming columnar grains. Interaction between migrating grain boundaries and inert gas bubbles causing the bubble to be swept along with the boundary has been reported
by several authors (123) (124) (125). There is also the possibility of a stress interaction effect with grain boundaries (58) (126) which may be significant under random migration conditions. The problem can easily be avoided in experimental investigations by observing regions well clear of the grain boundaries.

2.4.4 Temperature Gradients

The most important driving force for bubble migration in reactor technology is the temperature gradient. It is also, in principle, amenable to quantitative experimental analysis.

There has been some considerable confusion and misunderstanding in the literature about the phenomenon of thermal diffusion and the theory will be reviewed here in some detail.

The theory described here is concerned with the thermal diffusion effect in solids and is therefore concerned with volume diffusion. The applicability of this theory to surface diffusion and vapour transport bubble migration mechanisms will be discussed later.

a) Summary

The normal diffusion process is described by Fick's First Law:-

\[ J_1 = -ND_1 \nabla C_1 \]

When a temperature gradient is present:-

\[ J_1 = -ND_1 (\nabla C_1 + \frac{Q^*_1 C_1}{kT^2} \nabla T ) \]

\[ = \frac{-ND_1 C_1}{kT} (\nabla \mu_1 + \frac{Q^*_1}{T} \nabla T ) \]
where \( C_1 \) is site fraction of component 1
\( N \) is concentration of sites
\( D_1 \) is diffusion constant for component 1
\( Q_1^* \) is the effective heat of transport for component 1

\( V_{\mu_1} \) is the chemical potential driving 'force' due to the concentration gradient and the expression

\[
\frac{Q_1^*}{T} \cdot \nu T
\]

represents the 'force' exerted on component \( I \) by the temperature gradient.

Comprehensive reviews of the thermal diffusion phenomenon are contained in papers by Allnot and Chadwick (127) and Howard and Lidiard (128), the latter giving the thermodynamic approach.

b) Kinetic Approach to Thermal Diffusion

At thermodynamic equilibrium, the site fraction of vacancies:

\[
C_V = \exp \left( -\frac{h_v}{kT} \right)
\]

(14)

where \( h_v \) the heat of formation of a vacancy.

In an isothermal system the probability that an atom will jump to a particular adjacent vacant site:

\[
\omega (T) = \nu \exp \left( -\frac{\Delta h_m}{kT} \right)
\]

(15)

In the presence of a temperature gradient there will be a vacancy gradient and a bias to the jump probability:
\[
\frac{vC_V}{C_V} = \frac{h_v}{kT^2} \cdot vT
\]

\[
\omega(T, T + vT) = \omega(T) \left[ 1 + \Delta \omega(T) \cdot \Delta T \right]
\]

where \( \Delta T \) is the temperature difference between two adjacent sites in the direction of the temperature gradient and the equation defines \( \Delta \omega(T) \) a quantity which represents the biasing of the atomic jumps due to the temperature gradient.

From these equations Allnot and Chadwick (127) derive:

\[
J_l = -ND_l \left( \frac{q_l^* - h_v}{kT^2} \right) \cdot vT
\]

where \( q_l^* = \Delta h_m - 2kT^2\Delta \omega \) is the heat of transport for a single jump.

From this equation it can be seen that the flux of atoms resulting from a temperature gradient can be divided into two components, one due to the heat of transport the other to the vacancy concentration gradient.

Failure to realise this has caused some confusion, and the term heat of transport is often used to describe the resultant flux from both components. If this is done, the pre-fix 'effective' or 'measured' should be used in order to avoid confusion.

Shockley's (129) early discussion of this subject considered the vacancy gradient effect but did not include a heat of transport term. LeClaire (130) and Brinkman (131) recognised this error but took

\( \Delta \omega = 0 \) i.e. they assumed \( q_l^* = \Delta h_m \), and there is no reason to suppose that this is a reasonable assumption (Shockley (132)).

A similar analysis for thermally produced interstitial atoms
c) Thermodynamic Approach to Thermal Diffusion

The thermodynamic approach has been reviewed by Howard and Lidiard (128), Allnot and Chadwick (127) and Oriani (133).

The flux equations of irreversible thermodynamics are used (134) (135):

\[
J_i = \sum_{k=1}^{n} L_{ik} X_k + L_{iu} X_u \\
J_u = \sum_{k=1}^{n} L_{uk} X_k + L_{uu} X_u
\]

i and k ( =1 to n ) represent the various species present (atoms, interstitials, vacancies).

\( J_i \) is the flux of species \( i \) and  
\( J_u \) is the heat flux.

The coefficients \( L \) give the correlation of one flux with another and the \( X's \) are thermodynamic forces, which are given by the gradients of the rate of change of entropy with respect to the corresponding state variable (136) (137).

In order to establish an appropriate set of conjugate forces and fluxes, we write the Gibbs equation:
\[ dU = T \, ds + \mu_v \, dn_v \]

where \( \mu_v \) is the chemical potential of vacancies referred to some arbitrary reference state.

The vacancy flux:

\[ J_v = \frac{dn_v}{dt} \]

The heat flux:

\[ J_u = \frac{dU}{dt} \]

The conjugate vacancy forces (134):

\[ X_v = v \left( \frac{\partial S}{\partial n_v} \right)_U = - T \, \nabla \left( \frac{\mu_v}{T} \right) \]

\[ X_u = v \left( \frac{\partial S}{\partial U} \right)_{n_v} = T \, \nabla \left( \frac{1}{T} \right) = - \frac{v}{T} \]

Therefore, substituting into the flux equations for the case of a pure metal i.e. a single diffusion component, the vacancy, then:

\[ J_v = - L_{vv} \left[ T \, \nabla \left( \frac{\mu_v}{T} \right) + Q_v^* \, \frac{v}{T} \right] \]
where $Q_v^*$ is defined as

$$Q_v^* = \frac{L_{vu}}{L_{vv}}$$

and the Onsager reciprocity relation is used (136) (137):

$$L_{vu} = L_{uv}$$

If $VT = 0$ is substituted into these equations then:

$$J_u = Q_v^* \cdot J_v$$

This defines $Q_v^*$, the heat of transport for a vacancy, as the heat flux associated with a vacancy in an isothermal system.

Now, if local vacancy equilibrium is assumed ($c_v = c_v^o$) and $c_v^o$ is taken as the reference state for $\mu_v$ then:

$$V \left( \frac{\mu_v}{T} \right) = 0$$

and $J_v = -J_1$, $Q_v^* = -Q_1^*$

then:

$$J_1 = -\frac{N}{f} \frac{D_1}{kT^2} \cdot Q_1^* \cdot VT$$  \hspace{1cm} (18)$$

where $f$ is a correlation factor.
If the reference state for $\mu_v$ is taken to be some constant temperature independent vacancy concentration $c_v$, then:

$$V \left( \frac{\mu_v}{T} \right) = k_v \ln c_v$$

$$= h_v \frac{VT}{T^2}$$

(from equation (14))

Therefore

$$J = -\frac{N_D}{f kT^2} \left( Q^* - h_v \right) \cdot v T \quad (19)$$

Comparing (19) with (18)

$$Q^* = Q^* - h_v$$

Comparing (19) with (16)

$$Q^* - h_v = q^* - h_v$$

Therefore, if local vacancy equilibrium can be assumed, $Q^*$ represents the heat of transport that would be measured experimentally.

The simple relationship $Q^* = q^*$ is not necessarily found on comparing a thermodynamic and a kinetic equation, as such a relationship assumes a single diffusion mechanism.

There may be many diffusing defects (vacancies, vacancy pairs, interstitials etc) in which case $Q^*$ would be a function of the different $q^*$'s for the different jump processes.

The importance of the thermodynamic approach is that it establishes the true thermodynamic significance of the heat of transport.
i.e. \[ \mathbf{J}_u = Q_v \mathbf{J}_v \quad (\forall T = 0) \]

\[ = Q_1 \mathbf{J}_1 \quad (\forall T = 0) \]

d) Measurement of the Heat of Transport

Because of the unknown magnitude and sign of \( Q_1 \ast \) it is not possible to predict even the direction of the thermal diffusion or to distinguish between vacancy or interstitial transport mechanism by the measurement of \( J_1 \) contrary to Shockley's (129) original proposal. However, he did correctly predict that thermal diffusion can cause dimensional changes, and this forms the basis of the 'marker movement' experimental determination of the heat of transport.

Figure (4) illustrates the phenomenon. Relative to the lattice planes, the centre of mass of the material changes. If the ends of the system are taken as the static reference, then it is the lattice planes that move. New vacancies are formed from vacancy sources one end and excess vacancies removed at sinks the other end. The sinks and sources may be dislocations or grain boundaries, and the availability of these is an important point to consider in the analysis of experimental attempts to measure the heat of transport.

Such attempts have centred on 'marker movement' measurements. The principle of these experiments is to place a pair of markers in the crystal which remain fixed relative to the crystal planes of the lattice in the region of the marker. Since, in a temperature gradient, the two markers are at different temperatures, the corresponding thermal diffusion fluxes differ in magnitude. There is therefore either a gain or loss of matter between the two markers, and their distance apart should therefore
change by an amount which depends on the heat of transport.

Two forms of marker have been used. Shewmon (138) studied crystals and bi-crystals of zinc marked with indentations using a hardness machine. He did not find any dimensional changes. Swalin et al (139) repeated this experiment with certain extra precautions, and they found a contraction for zinc. A variation of the surface indentation procedure has been used for platinum (140), cobalt (141), lead and zinc (142) and lithium (143), Hatlock and Stark (144) have used the indentation technique with single crystal and polycrystalline samples of aluminium and they found

\[ Q^*_1 = +11 \text{ k cal/mole} \] for single crystals and

\[ Q^*_1 = -2 \text{ k cal/mole} \] for the polycrystalline samples.

The second type of marker consists of a thin filament of some inert material embedded in the crystal perpendicular to the temperature gradient. Kirkendall effect experiments (145) have given results independent of the form and kind of marker material, thus providing evidence for the validity of this technique. The first study of this kind was by Brammar (146) using 0.0015 in. diameter platinum wires in a - iron. No dimensional changes were found with a temperature gradient of 2500°C cm⁻¹. Meechan and Lehman (147) used a similar technique with silica fibres as markers, and they obtained,

\[ Q^*_1 = -4.8 \text{ k cal mole}^{-1} \] for gold and
\[ +3.0 \text{ k cal mole}^{-1} \] for copper.

The latter technique has proved to be very difficult. The major problems include obtaining sintered interfaces which are free from microscopic voids, machining the specimens without distorting them,
(specimen shape determined by the heating requirements for producing
the required steep temperature gradient) and removal of the specimens
from the annealing apparatus without bending them. The growth of grains
or twins in the vicinity of the marker may also perturb the progress of
the markers. Neeshan and Lehmann also observed void formation.

Another complication inherent in both techniques is the dif­
ficulty in evaluating the lattice accommodation coefficient $K$. If
the change in dimensions, due to the change in the number of atoms
between the markers, is isotropic, then $K = \frac{1}{2}$, but if the changes
only occur in the direction of the temperature gradient then $K = 1$.
At present no generally agreed way of predicting $K$ exists, and the
problem is complicated by the different specimen shapes found in thermal
diffusion experiments. The problem has been discussed by Huntington and
Grone (148) and da Silva and Mehl (145) with regard to Kirkendall experi­
ments, Penney (149) with regard to electromigration studies in aluminium,
Ho et al (140) and Jaffe and Shewmon (150) with regard to thermal self­
diffusion experiments. With anisotropic metals such as zinc the problem
is further complicated (151) (139).

Most of the problems discussed so far with regard to marker
movement thermal diffusion experiments have some relevance to a bubble
migration experiment, but there is little doubt that the most serious
problem for both types of investigation is the question of the efficiency
and availability of vacancy sources and sinks. The assumption of local
vacancy equilibrium in a vacancy gradient requires that the necessary
sources and sinks are available and can either produce or sink vacancies
at a sufficient rate to maintain equilibrium. If the available sources
and sinks cannot maintain local vacancy equilibrium then there will be
a reduced vacancy flux. In the case of surface diffusion the same
argument can be applied to surface vacancies or adatoms.
In the extreme case, a stationary state \( (j^1 = 0) \) could be set up where the low vacancy production and destruction rates have produced a vacancy gradient in opposition to the thermal diffusion flow, i.e.:

\[
\nabla \mu_v = \frac{Q_1^*}{T} \cdot \nabla T
\]

where

\[
\nabla \mu_v = kT \nabla \ln c_v
\]

\[
= kT \frac{\nabla c_v}{c_v}
\]

therefore

\[
\frac{\nabla c_v}{c_v} = \frac{Q_1^*}{kT^2} \nabla T \tag{20}
\]

The above equation refers to the extreme case. Blackburn \(^{(152)}\) and Fatlock and Stark \(^{(144)}\) have produced analyses of the intermediate situation that would normally be found in reality.

Blackburn \(^{(152)}\) has derived:

\[
J_1 = J_1^0 \frac{c_v}{c_v^0}
\]

where

\[
\frac{c_v - c_v^0}{c_v^0} = \left[ \frac{h_v (h_v + \nabla h_v - Q_1^* - 2kT) - Q_1^* (\nabla h_v - 2kT)}{kT^2} \right] \cdot \frac{\lambda \nabla T}{kT^2}
\]
where $\lambda$ is the mean free path of a vacancy between creation and annihilation.

Matlock and Stark (144) have derived:

$$J_1 = \frac{aHD_1}{kT^2} \left( Q_1^* - \gamma h_v \right) v T$$

where $a$ corrects for the influence of the non-equilibrium vacancy concentration of the diffusion coefficient, and

$$a = \frac{c_v}{c_v^0}$$

and $\gamma$ lies between 0 and 1 if $Vc_v$ lies between 0 and its equilibrium value.

Blackburn's equation is in direct conflict with (20) in that it predicts that $J_1 = 0$ only if $c_v = 0$, and this does not seem reasonable.

A similar argument can be applied to Matlock and Stark's analysis, if the value of $\gamma$ is restricted to the range quoted by the authors. In fact there is no reason why $\gamma$ should not be negative or $> 1$.

Even though these analyses are relevant to the real situation they do little more than tell us that the measured diffusion flux is intermediate between the value derived for local vacancy equilibrium conditions and zero. Blackburn's analysis introduces a quantity $\lambda$ and Matlock and Stark's quantities $\alpha_H'$, $\alpha_C$ (hot and cold ends of specimen, $\gamma$ is a function of $\alpha$) which cannot be evaluated. The latter authors experimental results ($\lambda_1^* = +11 k$ cal mole$^{-1}$ for Al single crystal and $\lambda_1^* = -2 k$ cal mole$^{-1}$ for Al polycrystals)
strongly suggest that grain boundary vacancy sources are the dominant factor determining the apparent value of $Q^*_1$. They considered the possibility of a negative heat of transport for grain boundary diffusion as a possible alternative explanation for their results, but concluded that it was not a reasonable explanation.

The experimentally determined values for the heat of transport for various metals are summarised in Table I.

e) Atomistic Theories for the Heat of Transport

The atomistic theories for the heat of transport have been reviewed by Allnott and Chadwick (127) and Oriani (133). It is evident that there is no satisfactory theory available and that theoretical estimates of the magnitude of the heat of transport are restricted to generalisations as to the range of values within which the heat of transport should lie.

The first of these analyses was due to Wirtz (160). He proposed that $\Delta h_m$ could be divided into three parts $\Delta h_1$, $\Delta h_2$, and $\Delta h_3$, these energies being supplied respectively at the initial position of the jumping atom, at the intermediate plane and at the final position where the atoms surrounding the vacancy must be pushed back to accommodate the jumping atom. The temperatures at these three positions are taken as $T$, $T + \frac{\Delta T}{2}$, and $T + \Delta T$. This analysis leads to the result:

$$q^*_1 = \Delta h_1 - \Delta h_3$$

The exact significance of the three enthalpies is by no means
clear, and have been interpreted in different ways by different workers. Nevertheless, this model does make one quantitative prediction:

\[ q^* \leq A h_m \]

It is not obvious that this is a reasonable prediction, and there is experimental evidence (see Table I) that suggests that this is not true.

There are many other models which are reviewed by Allnott and Chadwick (127) and Oriani (133) none of which are particularly satisfactory and most of which bring in variables related to the energy distribution before, during and after the atomic jump which cannot be evaluated. Oriani (133) concludes that any model which depends explicitly upon \( vT \) for its mechanism and which cannot be applied to the isothermal case does not correctly represent the physics of thermomigration. This criticism applies to many of the published theories. One of the major advantages of the application of irreversible thermodynamics to this problem is that it describes the significance of the heat of transport in isothermal and anisothermal conditions.

The large \( Q_1^* \) values for platinum, cobalt, \( \beta \)-zirconium and \( \beta \)-titanium have attracted some theoretical attention (141) where an electron flux mechanism is suggested.

f) Significance of \( Q_1^* \) in Bubble Migration

This will be treated in more detail in a later section where bubble velocities for certain diffusion mechanism-driving force combinations will be presented.
As a general statement, it is concluded that a temperature gradient provides an atomic driving force:

\[ f = - \frac{Q_1^*}{T} \nabla T \]  \hspace{1cm} (21)

where \( Q_1^* \) is the measured heat of transport and

\[ Q_1^* = Q_1^* - h \]

where \( Q_1^* \) is the heat of transport for the atomic jump.

Some of the early analyses of bubble migration in a temperature gradient did not introduce the concept of a heat of transport at all \((64)\) \((65)\). They argued that an atom moving in a temperature gradient changes its energy by \( \Delta E \), where:

\[ \Delta E = 3k \Delta T \]

The atomic driving force would therefore be:

\[ f = \frac{\Delta E}{\Delta x} = -3k \nabla T \]

therefore

\[ Q_1^* = 3kT \] (the equilibrium internal energy)

independent of diffusion mechanism.

This is clearly not true. As Oriani \((161)\) has pointed out, \( Q_1^* \) may be viewed as the amount by which the average energy of the migrating species exceeds the enthalpy of the surrounding matrix. It must, therefore, be dependent upon the diffusion mechanism. Nichols \((52)\) points out that
Q^* = 0 for the vapour diffusion component of the vapour transport void movement mechanism, and therefore the 'effective' heat of transport:

\[ Q_E^* = \Delta H_v \]

where \( \Delta H_v \) is the heat of vaporisation of the matrix material.

As Nichols (52) points out, the vapour transport mechanism is the only mechanism for bubble migration where the value of the effective heat of transport can be predicted. For volume diffusion and surface diffusion the values of \( Q_b^* \) and \( Q_v^* \) cannot be predicted either in sign or magnitude. Experimental evidence suggests that values of both sign are found for various systems for the volume diffusion case and experimental information available for bubble migration (see Section 7) where a surface diffusion mechanism appears to be operative indicate that the effective heat of transport \( Q_s^* \) is positive i.e. the bubbles move up the temperature gradient.

2.5 Velocities of Bubbles under Biasing Driving Force

2.5.1 Bubble Mobility Approach

To obtain the velocity of a spherical bubble \( V_b \), assuming it maintains its shape while migrating, one applies the drift velocity equation:

\[ V_b = B_B \frac{F_B}{kT} \]

where \( B_B = \frac{D_B}{kT} \) = bubble mobility
and \( F_B \) is the force applied to the bubble. This technique has the advantage of being flexibly applied to a range of diffusion mechanisms and driving forces compared with the many examples in the literature of velocities calculated for particular diffusion mechanism driving force combinations.

Now equation (21) gives the atomic driving force due to a temperature gradient, and the bubble force is required. The atomic driving force \( f \) can be related to the equivalent force \( F \) on the bubble by considering the work done by the force \( F \) in moving the bubble a distance \( \ell \). This work \( (F \ell) \) is equivalent to the work done by the force \( f \) in moving an equivalent number \( \left( \frac{4}{3} \pi r^2 / \Omega \right) \) of atoms a distance \( \ell \) in the opposite direction.

It follows that

\[
f = -\frac{3 \Omega}{4 \pi r^3} F
\]

therefore

\[
V_B = -\frac{D_B}{kT} \cdot \frac{4 \pi r^3}{3 \Omega} \cdot f \tag{VBL}
\]

For a temperature gradient

\[
f = -\frac{Q_s^*}{T} \cdot \nabla T
\]

For the surface diffusion mechanism

\[
D_B = \frac{3}{2} \frac{\Omega^2 \nu D_s}{\pi r^4}
\]
\[ V_{BS} = \frac{2 D_S \nu \Omega \frac{Q_s^*}{kT}^2}{r} \cdot \nabla T \]

where \( Q_s^* \) is the heat of transport for the surface diffusion mechanism.

Nichols (52) points out that a correction factor \( \beta_S \) should be included in the above equation as initially pointed out by Biersach and Dies (162) for the volume diffusion mechanism due to the perturbation of the temperature gradient in the region of the bubble:

\[ V_{BS} = \beta_S \cdot \frac{2 D_S \nu \Omega \frac{Q_s^*}{kT}^2}{r} \cdot \nabla T \quad (22) \]

A similar analysis for volume diffusion mechanism and temperature gradient gives:

\[ V_{BV} = \beta_V \cdot \frac{D_V \frac{Q_v^*}{kT}^2}{r} \cdot \nabla T \quad (23) \]

And for vapour transport, temperature gradient:

\[ V_{BV_T} = \beta_{VT} \cdot \frac{D_{VT} \Omega \alpha P \frac{\Delta H_v}{k^2 T^3}}{r} \cdot \nabla T \quad (24) \]

where \( Q_{VT}^* = \Delta H_v \)

and \( D_{VT} \sim r \) for a bubble.

Therefore, for the case of a temperature gradient, surface diffusion control leads to \( V_B \sim r^{-1} \) and volume diffusion leads to a velocity which is independent of \( r \). Vapour transport yields a velocity independent of \( r \) for \( p = P_v \) (i.e., for a void) and \( V_B \sim r \).
It is clear that surface diffusion will dominate at small bubble sizes and that as the size increases either volume diffusion or vapour transport will become dominant. Also since normally $\Delta H_V > Q_V > Q_S$, where $Q_V$ and $Q_S$ are the activation energies for volume and surface diffusion, then as the temperature increases the dominant mechanism could shift from surface diffusion to volume diffusion to vapour transport.

For the other driving forces (stress gradient, dislocation and grain boundary) the bubble mobility approach is the only viable technique available as analyses using the more fundamental atomic mobility approach would be too complex and in the case of dislocations and grain boundaries would require a precise knowledge of the geometry of the interaction.

2.5.2 Atomic Mobility Approach

This approach has already been described in the calculation of $D_B$ for surface diffusion by Gruber (68) and Shewmon (67). The approach using bubble mobilities requires the assumption that spherical pores move as spheres whereas the atomic mobility approach allows an assessment of the validity of this assumption; that is, we start with a spherical bubble, apply an atomic driving force and calculate the drift velocity of the bubble surface as a function of the position on that surface.

It is required to calculate the outward normal rate of motion of the surface ($\frac{dp}{dt}$) for the three diffusion mechanisms.

For volume diffusion and vapour transport it is simply:

$$\frac{dp}{dt} = -j \Omega \quad \text{(volume)}$$

$$= j \Omega \quad \text{(vapour)}$$
where \( j \) is the flux normal to the surface of the bubble.

For surface diffusion, the system is less straightforward as the surface flow is parallel to the surface, but it is the consequent normal component which results in bubble movement.

Consequently \((68)\):

\[
\frac{dp}{dt} = -\frac{2 \Omega^{\frac{1}{3}} D_{s} Q_{s}^{*}}{\kappa T} \cos \theta \cdot \frac{Q_{s}^{*}}{T} \cdot v_{T}
\]

\[
= -\left[ \frac{2 \Omega^{\frac{1}{3}} D_{s} Q_{s}^{*}}{\kappa T^{2} r} \right] \cos \theta
\]

It can be shown that the form of the above equation means that:

\[
V_{BS} = \frac{2 \Omega^{\frac{1}{3}} D_{s} Q_{s}^{*}}{\kappa T^{2} r} \cdot v_{T}
\]

and that the bubble remains spherical.

The above equation assumes that \( v_{T} \) for the bubble is the same as \( v_{T} \) for the bulk of the matrix. The atomistic analysis of the volume diffusion case by Biersach and Diez \((162)\) highlighted this error as it is particularly significant in the case of volume diffusion. For volume diffusion, \( v_{T} \) in the matrix \( (v_{T_{m}}) \) must be resolved normal to the bubble surface.

i.e. \( (v_{T_{m}})_{N} = v_{T_{m}} \cos \theta \)

therefore

\[
\frac{dp}{dt} = j \Omega = \left[ \frac{D_{v} Q_{v}^{*} v_{T_{m}}}{\kappa T^{2}} \right] \cos \theta
\]
therefore

\[ V_{BV} = - \frac{D_v Q_v^*}{kT^2} \sqrt{v} T_m \]

where \( V_{BV} \) is the bubble velocity with respect to the lattice. But volume diffusion represents a special case because the lattice itself is moving with a velocity given by:–

\[ V_e = \frac{D_v Q_v^*}{kT^2} \sqrt{v} T_e \]

The bubble velocity with respect to an external marker (Biersach and Dies call this an end face reference) the velocity is:–

\[ V_B = \frac{D_v Q_v^*}{kT^2} \left( \sqrt{v} T_e - \sqrt{v} T_m \right) \]

Therefore if the conductivities of the matrix and the bubble were equal then \( V_B = 0 \).

If the matrix conductivity is \( k \) and that of the bubble is \( k' \) then:–

\[ \sqrt{T_B} = \frac{3k}{2k + k'} \sqrt{T_e} \quad \text{(in bubble)} \]

\[ \sqrt{T_m} = \left[ 1 - \frac{2(k - k')}{2k + k'} \right] \sqrt{T_e} \quad \text{(in matrix)} \]

(Carslaw and Jaeger (163)).

From this, the constants \( \beta \) mentioned in the previous section can be evaluated (52):–
\[ \beta_s = \beta_{VT} = \frac{3k}{2k + k'} \]
\[ \beta_v = \frac{2(k - k')}{2k + k'} \]

therefore
\[ V_{BV} = \frac{D_v Q_v^*}{kT^2} \cdot \left[ \frac{2(k - k')}{2k + k'} \right] \frac{V_T}{\gamma} \]

Similarly, for the vapour transport case:
\[ \frac{3p}{\delta t} = -\left[ \frac{D_{VT} \Omega \alpha_v p_v \Delta H_v}{k^2 T^3} \cdot \frac{V_T}{\gamma} \right] \cos \theta \]
and
\[ V_{BVT} = \frac{D_{VT} \Omega \alpha_v p_v \Delta H_v}{k^2 T^3} \cdot \left[ \frac{3k}{2k + k'} \right] \frac{V_T}{\gamma} \]

For surface diffusion:
\[ V_{BS} = \frac{2 D_s \Omega \frac{1}{2} Q_s^*}{kT^2} \cdot \left[ \frac{3k}{2k + k} \right] \frac{V_T}{\gamma} \]

For a bubble, it is reasonable to put \( k' = 0 \)

Therefore
\[ \beta_s = \beta_{VT} = \frac{3}{2} \]
\[ \beta_v = 1. \]

It is interesting to note that in the volume diffusion case the direction of motion is dependent on the relative conductivities \( k \) and \( k' \).
A spherical particle with a higher conductivity than the matrix would travel in the opposite direction to a gas filled bubble or void.

2.6 Theories of Migration and Coalescence

Theories of migration and coalescence of inert gas bubbles have been proposed by Barnes (164), Speight (165), Gruber (166) and Baroody (166) and Wolfenden and Farrel (167) have considered migration and coalescence as a possible mechanism for the coarsening of grain boundary bubbles in CVD tungsten.

These theories are based on the assumptions that the bubbles migrate by surface diffusion, that there is no re-solution of gas from the bubbles, that the gas behaves ideally and that the gas pressure is in equilibrium with the surface tension of the surrounding matrix. It is also assumed that there are no bubble interactions except immediate coalescence on contact and in some of the analyses that the bubble distribution can be characterised by a mean bubble radius.

Barnes' treatment assumes that Brownian motion will be insignificant due to the restraining influence of dislocations and that stressed dislocations will provide the driving force producing migration. Migration along the dislocation lines of randomly situated bubbles is mentioned, near neighbours experiencing convergent forces, but is not taken into consideration in the analysis. A constant driving force $F = \mu b^2$, where $\mu$ is the shear modulus and $b$ the Burgers vector, a bubble diffusion coefficient $a r^{-4}$ for a surface diffusion mechanism and a final bubble radius large enough for the initial radius $r_0$ to be ignored ($r^4 \gg r_0^4$) are assumed giving a bubble radius $a t^4$, where $t$ is the annealing time.
Most analyses have assumed that Brownian motion is the dominant cause of migration, with the possibility of dislocations and grain boundaries acting as traps. Such analyses would seem to be more appropriate for the annealing of helium ion implanted metals where the structure has been stabilised by annealing before ion implantation.

The analyses of Speight, developed from a theory of swelling by Greenwood and Speight, and Wolfenden and Farrell, are based on the calculation of a coalescence time. Wolfenden and Farrell, calculated the interaction area swept out by the bubble as it migrates in the grain boundary in the same way that Barnes calculated the interaction volume for migration through the lattice. They then applied the random motion diffusion equation:

\[ t = \frac{x^2}{2D_Bi} \]  

(25)

where \( t \) is the average time for a bubble to diffuse a distance \( x \), \( D_B \) is the bubble diffusion coefficient and \( i \) is the number of degrees of freedom available for bubble translation.

The applicability of this equation when used to calculate interaction areas (or volumes) in 2 (or 3) dimensional system is somewhat doubtful. It does not represent the distance swept out by the bubble, but merely gives the average distance from the starting point after time \( t \). It can therefore only be applied to one-dimensional diffusion e.g. along a dislocation line. The analytical technique used by Wolfenden and Farrell applied to the 3-dimensional case gives an equation of the form:

\[ t_c \propto r^4 \]

where \( t_c \) is the coalescence time.
Greenwood and Speight (64) use a somewhat artificial model incorporating equation (25) and derived an equation of the form:--

\[ t_c \alpha r^5 \]

Speight (165) used the above coalescence time and calculated the total heat treatment time as the sum of the times for successive coalescences, a geometric series, giving:--

\[ t = \frac{(r^5 - r_0^5)}{k} \]

where \( k \) is a constant

\[ i.e. \ r \propto t^{1/5} \text{ when } r^5 >> r_0^5 \]

It would appear that the relationship between average bubble radius and annealing time as derived by means of the calculation of a coalescence time is very dependent on the details of the model chosen, and that the use of equation (25) for this type of calculation is not correct.

A more rigorous analysis has been that due to Gruber (68). This theory is based on the analogous problem of colloid coagulation as treated by Chandrasekhar (168) who derived:--

\[ J_{i+k} = 4 \pi D_{ik} \cdot R_{i} \cdot v_i \cdot v_k \left( 1 + \frac{R_{ij}}{v D_{ik} t} \right)^{1/2} \]  (26)

In the case of bubble coalescence \( J_{i+k} \) is the coalescence rate between bubbles of radius \( r_i, r_j \); \( v_i \) and \( v_k \) are the respective concentrations of these bubbles and \( R_{ij} \) is the interaction distance \( (r_i + r_j) \). The diffusion coefficient \( D_{ik} \) is shown by Chandrasekhar to
be given by \((D_i + D_k)\). If the mean distance travelled by the two bubbles relative to one another is large compared with the sum of the bubble radii, then the term in brackets at the end of equation (26) can be neglected.

\[
J_{i+k} = 4\pi (D_i + D_k) (r_i + r_k) \nu_i \cdot \nu_k
\]  

(27)

Using this equation, Gruber\(^{(68)}\) has produced a computer based analysis. These calculations together with a subsequent curve fitting technique gave an equation for the average radius:

\[
r = 1.30 \left[ \frac{m k T a_0^4 D s t}{\gamma} \right]^{1/5}
\]  

(28)

where

- \(m\) is the gas concentration
- \(a_0\) is the interatomic distance
- \(D_s\) is the coefficient of surface self diffusion.

The initial bubble size is assumed to be the monatomic gas atom.

Baroody\(^{(166)}\) has carried out a similar analysis to that of Gruber but it is analytical rather than computer based. Several approximations and assumptions are made in this analysis which in general agrees with the results of Gruber’s analysis.

The most significant feature of the analyses of Gruber\(^{(68)}\) and Baroody\(^{(166)}\) is that they do not approximate to an average radius but actually calculate what the bubble size distribution is. The result is most clearly presented by Gruber with his standardised size distribution function for random coalescence plotted against number of atoms in the bubble multiplied by a 'reduced time' variable which is a function of annealing time, inert gas concentration and annealing temperature. The main weakness with both Gruber’s and Baroody’s analyses when applied to
situations of reactor technology interest is the assumption of ideal gas behaviour which can introduce serious errors when applied to bubbles with radii less than 1000Å.

All these theories assume that motion is random and that structural heterogeneities are not influencing the behaviour. This, of course, is unlikely in reality. Speight (165) has modified his analysis for migration and coalescence for the situation where bubbles are restrained to move along dislocation lines. He derives an average radius proportional to $t^{1/7}$. Beéré (80) has also analysed such a restrained migration for the specific case of a thin foil.

2.7 Experimental Techniques and Results

There is only a limited amount of experimental information available concerning bubble mobility and no clear verification of the mobility theory is available.

The techniques can be divided into two classes, direct and indirect. Indirect techniques are those where bubble diffusion behaviour is deduced from gas release studies and these have been reviewed in an earlier section. This is not a satisfactory technique for studying bubble behaviour as these studies are so severely affected by surface and irradiation damage effects; it is an unfortunate feature of gas release work in that it is usually carried out in a region which is uncomfortably close to the surface. Indirect techniques cannot be satisfactory when so many complicating factors are present and the scatter in diffusion coefficients for inert gas diffusion obtained by these techniques is a clear indication of the unreliability of the technique.
The direct techniques can be divided into three classes:-

i) migration distance studies

ii) migration and coalescence studies

iii) applied driving force techniques.

The first experimental information to become available used the applied driving force technique, and this was by Barnes and Mazey (26) who pulse heated a copper foil containing helium bubbles in the electron microscope and found that the migration velocity of small \( r < 1000\,\mu\text{m} \) bubbles was \( V_B \propto r^{-1} \) suggesting that surface diffusion was the mechanism for migration.

2.7.1 Migration Distance Studies

This technique has been used by Cornell and Bannister (77) and Gulden (79) for \( \text{UO}_2 \), Walker (78) for stainless steel, Beere (80) for copper and Willertz (70) for gold and copper, and all have used ion implanted foils except Gulden who used reactor irradiated uranium dioxide.

For this technique identical areas of thin foil containing inert gas bubbles are examined before and after annealing in an electron microscope. By superimposing films the r.m.s. migration distances are measured and the bubble diffusion coefficient can be calculated from:

\[
x^2 = 4\,Dt \quad (2\text{ dimensional system})
\]

The factor 4 is used in this equation because the measurements are not three dimensional i.e. stereo photographs were not taken and therefore only the 2-dimensional component of the random migration is being measured. In the case of Beere's investigation the one dimensional
was used as he was specifically measuring bubbles migrating along dislocations.

There are several objections to this technique:

i) the entire investigation is carried out in a thin foil of thickness less than 2000Å and therefore the bubbles are always close to a free surface. Willis and Bullough (57) and Lieden and Nichols (58) have shown theoretically that a bubble with uncompensated gas pressure will be attracted to a free surface and Lidiard and Nelson (59) have pointed out that an equilibrium bubble can still have a strain field associated with it due to the distinction between surface energy and surface tension giving an effective uncompensated gas pressure which is a function of the difference between the surface energy and surface tension values. It is therefore likely that bubbles close to a surface will not exhibit random migration but will be biased towards it. This objection would not apply to work carried out in a high voltage microscope (1 MeV).

ii) there is a contamination hazard when annealing thin foils because of the high surface area to volume ratio. The hazard applies both to the annealing furnace and the electron microscope. Contamination built up on the specimen surface during observation in the microscope may be dissolved into the foil during a subsequent annealing treatment.

iii) there is a danger of distortion and deformation of the foils during handling and annealing which could lead to undesirable stresses and dislocation interactions. For example, Willertz mounted his foils on tungsten grids and therefore differential expansion between foil and grid could cause deformation.
iv) Bubbles which have migrations on the large side of the distribution which makes up \( \frac{1}{x^2} \) are more likely to disappear due to contact with a surface and will therefore not be included in the distribution. This effectively makes the observed R.M.S. distance smaller than it should be.

Cornell and Bannister \(^{(77)}\) implanted 100 keV Kr\(^+\) ions into uranium dioxide precipitated into bubbles ranging from 40\(^\circ\) to 130\(^\circ\) radius. Their measurement of r.m.s. migration distances at 1500\(^\circ\)C and 1600\(^\circ\)C gave:

\[
(\frac{1}{x^2})^\frac{1}{2} = r
\]

which does not agree with any of the models for bubble migration.

Gulden \(^{(79)}\) carried out a similar investigation with irradiated uranium dioxide and found:

\[
(\frac{1}{x^2})^\frac{1}{2} = r^{-3/2}
\]

indicating a volume diffusion controlled mechanism, and the migration rate was much slower than would have been expected if a surface diffusion mechanism had been operative. Studies with reactor irradiated uranium dioxide are complicated by the presence of solid fission products, and the micrographs used by Gulden showed precipitate particles in the bubbles. It is quite likely that contamination has inhibited surface diffusion.

Walker \(^{(78)}\) carried out a similar investigation with helium ion implanted stainless steel and found a mobility which had a maximum at a radius of 5 \(x 10^{-3}\) \(\mu m\) independent of annealing temperature. The movement of bubbles larger than this optimum mobility size was considered characteristic of volume diffusion controlled migration.
Willertz (70) and Willertz and Shewmon (71) have carried out migration measurements on copper and gold foils. They used two techniques for measurement. One was to measure the rate of loss of bubbles to the foil surface due to the random migration and the other was the measurement of r.m.s. migration distances. Their results for gold were a factor of $10^4 - 10^5$ lower than expected from surface diffusion data and a factor of $10^2$ lower than expected for copper. The results using both techniques showed considerable scatter and consequently it is difficult to have much confidence in these results. The r.m.s. technique gave bubble diffusion coefficient values approximately $\frac{1}{20}$ of that by the rate of escape technique. Several aspects of the experimental technique used cause concern about the validity of the results. For example, the ion implantation of the foils was carried out using the un-analysed beam direct from an ion source, which particularly with helium with its low ionising efficiency will inevitably result in a substantial impurity content to the beam. This impurity component is important for two reasons; it introduces an impurity component into the foil which can be of critical importance where any type of surface diffusion process is involved and it can also cause unnecessary irradiation damage. This latter consideration would not be important if the heavier inert gases were being implanted, but nevertheless one of the main advantages of helium is the low energy and low damage caused by implantation to a certain depth compared with heavier elements. It is also suggested that the pre-irradiation anneals used in this work were probably not sufficient to lower the defect density to acceptable values and the standard of vacuum cleanliness during the anneals also seems open to doubt (on the author's admission).

The considerable difference between the measured and calculated mobilities in the gold foils is explained in terms of interface controlled
mobility and this has been discussed in a previous section.

Beere (80) has investigated the migration of inert gas bubbles along dislocations in copper foils, estimating the bubble diffusion coefficient by r.m.s. migration measurements and bubble loss measurements. The r.m.s. measurements suggested that the migration distance reached a maximum for bubbles of 10 nm \((100^\circ)\) radius, but this was deduced to be due to the foil dimensions, not a real effect. The relationship between bubble diffusion coefficient and radius varied with radius but was approximately \(D_B \propto r^{-8.5}\) for \(r > 10\) nm. The migration velocity was approximately 30 times slower than calculated from surface diffusion measurements. It was concluded that the rate controlling mechanism for bubble migration along dislocations was the nucleation of fresh atomic planes on the bubble surface, and that the dislocation reduces the critical nucleation energy and therefore increases the bubble mobility compared with bubbles not on dislocations.

2.7.2 Migration and Coalescence Studies

Migration and coalescence studies have been carried out by Vela and Russell (37) in copper-boron alloys and Hudson (169) in uranium. Both of these investigations were carried out with irradiation produced inert gases.

Vela and Russell (37) found \(r \propto t^{1/14}\) for helium bubbles in a copper - 0.04 wt \(\%\) boron-10 alloy irradiated to produce 0.05 at \(\%\) helium. They found that the bubbles were all nucleated on dislocations and there was no evidence of homogeneous nucleation. Areas of foil free of dislocations were also free of bubbles. Pulse heating experiments failed to produce the bubble migration found by Barnes and Hazey (26) in copper. They
concluded that the presence of 0.05 at% lithium and some residual boron together with the pinning effect of the dislocations was combining to produce behaviour significantly different to that in copper.

Hudson (159) obtained similar results for fission gas bubbles in uranium, with a bubble density proportional to t^{-1/6} at 800°C (equivalent to r = t^{1/12}) and a rate of bubble growth much slower than expected. It is interesting to note that contrary to expectations, small bubbles (~50Å diameter) in α-uranium did not appear to be easily swept by passing dislocations, as annealing under a stress sufficiently high to produce rupture after 32 hours at 600°C did not change the bubble size distribution from that found in an unstressed specimen.

2.7.3 Applied Driving Force Techniques

There are four significant bubble driving forces present in a reactor environment which can have a significant influence on the bubble size distribution. These are:-

1. temperature gradient
2. stress gradient
3. dislocation movement
4. grain boundary movement

The first of these is the one that has received most theoretical attention and is the most suitable driving force for an experimental investigation. Experimentally the problems are by no means trivial. Large, stable and well defined temperature gradients of the order of 1000°C cm^{-1} are not easily achieved and as a consequence much of the experimental information available has come from the semi-quantitative pulse heating techniques.
a) **Pulse heating techniques**

This technique was first used by Barnes and Mazey (26) to produce migration of helium bubbles in copper foils. The foil is pulse heated in the transmission electron microscope by removing the condenser aperture for intervals of several seconds so that a temperature gradient is produced during the pulse and Barnes and Mazey showed the migration velocities of the bubbles were approximately proportional to $r^{-1}$, which is consistent with a surface diffusion mechanism.

This technique is useful for giving this type of information i.e. radius dependence of migration velocity which can enable the diffusion mechanism to be established, but because of the unknown magnitude of the temperature and temperature gradient it cannot yield any quantitative information.

Cornell and Williamson (170) have used this technique for ion implanted krypton bubbles in $UO_2$ and they found $v \propto r^{-1}$ as predicted for surface diffusion. Similar experiments by Manley (171) confirmed this relationship for irradiation produced inert gas bubbles, but it was found that some of the bubbles were associated with small precipitates thought to contain fission products and were as a consequence less mobile than free bubbles.

In contrast Barnes and Mazey (172) reported work on uranium dioxide foils that showed no discernable dependence of mobility on bubble size, but these foils were prepared by oxidising uranium foils in the electron microscope. The authors suggest that the non-stoichiometry of the uranium dioxide formed in this way may influence the results.

Wilsonham (41) did not report a radius dependence relationship but he estimated that $100 \AA$ diameter bubbles in uranium dioxide were moving
with a velocity $= 10^3 \text{ A}^0 \text{ sec}^{-1}$ at a temperature of $= 1600^\circ\text{C}$ and a gradient of $= 10^6 \text{ oC cm}^{-1}$.

Reudl and Kelly (173) (174) have reported bubble migration in pulse heated foils of platinum and silver.

b) Controlled Temperature Gradient Techniques

The first investigation of bubble migration in a controlled temperature gradient was by Selleck and DeCrescente (85). They implanted 100 keV helium ions into cylindrical specimens of uranium carbide, annealed to produce helium bubbles and subjected to a temperature gradient of $900^\circ\text{C cm}^{-1}$ by heating one end with an electrically heated tungsten bar and the irradiated face at the other end losing heat by radiation. The sample was then fractured and examined by replica techniques. The bubbles were found to have migrated up the thermal gradient with a velocity proportional to $r^{-1}$, the bubble radii being in the range 300-2500$. This indicates a surface diffusion mechanism in the temperature range investigated (700-1500$^\circ\text{C}$).

Similar work has been reported by Weaver (175) for uranium nitride. The size dependence was not reported, but the bubbles moved up the temperature gradient, implying, as with the uranium carbide investigation, that $Q_{-1} > 0$.

Oldfield and Brown (84) have studied the migration of lenticular 'bubbles' in uranium dioxide. A hemi-spherical specimen shape was used with the curved surface cooled either by contact with a water cooled block or by radiation loss and the centre of the flat face was heated by a laser beam of up to 20 watts power. Computer calculations were used to calculate the temperature distribution in this specimen geometry. The temperature of the hot surface of the specimen was estimated by two
techniques; at high power levels the onset of surface melting was used for temperature calibration and at lower power levels the rate of evaporation of the uranium dioxide was used.

The 'bubbles' investigated by Oldfield and Brown are not gas filled spherical bubbles but are lenticular voids resulting from the porosity of the UO₂, which was typically about 80% theoretical density. Although this study is useful for the study of nuclear fuel behaviour it is somewhat different to the problem of migrating near-spherical gas filled bubbles. These lenticular voids were large (about 2μm), of unknown surface purity and gas content and were always associated with a grain boundary. Indeed, the measurement of the length of the columnar grain in the trail of the void is the migration distance measurement technique. The measured migration velocities were much slower than would be predicted by any of the diffusion controlled migration mechanisms. They concluded that the development of new ledges on the condensing surface was the limiting process. Surprisingly they did not suggest that the association with a grain boundary might have some significant effect on the migration velocity.

Buescher and Meyer (85) have reported what is probably the most precise experimental investigation of bubble movement in a temperature gradient. 14 MeV He⁺ ions were implanted into uranium dioxide single crystals which were then heat treated to give bubble precipitation. These single crystals were then embedded into sintered uranium dioxide pellets (1 cm diam right cylinders) which were then suitable for mounting in a temperature gradient furnace (176). Small black body holes were drilled in the side of the pellet to permit accurate pyrometer sightings. After the temperature gradient anneal the samples were sectioned parallel to the axis of the cylindrical pellet, polished and etched, and dark field
micrographs taken. The bubbles were visible in a fine line, which was reddish in colour, \( \approx 5 \mu m \) wide and between 57 and 68 \( \mu m \) beneath the implanted surface. Fractured surfaces of the samples that contained the bubble line were examined using the scanning electron microscope in order to measure the bubble size distribution.

They found that the bubbles advanced up the temperature gradient with a constant velocity independent of bubble size. Volume diffusion would predict this lack of bubble size dependence but the measured velocities were \( 10^6 \) times too fast. Surface diffusion and vapour transport would both lead to a size dependence which was not found. The results were in reasonable agreement with Michels and Poeppel's \(^{(177)}\) in reactor bubble velocity measurements in a mixed oxide fuel measured by a trail length technique. They propose that a mechanism of surface diffusion affected by collisions with the gas atoms in the bubble is operative and this has been discussed in a previous section.

Several other temperature gradient investigations have been carried out on transparent materials such as alkali metal halides and camphor \(^{(178-186)}\), but these investigations tend to generate problems peculiar to the system being studied and in general do not seem to be of much help in the understanding of bubble migration in reactor environments.

There do not appear to be any published results of temperature gradient migration velocities for controlled gradients in any metal.

2.8 Summary

The main conclusions to be drawn from the literature survey are:

1. The available solubility evidence suggests that inert gases can be regarded as being 'insoluble' in metals, and that bubbles will be stable and will not lose inert gas atoms by a solution mechanism.
Inert gas diffusion studies show that once precipitation into bubbles has occurred then the trapping is permanent.

(ii) Bubbles in metals have an equilibrium size determined by the balance between surface tension and internal gas pressure and will in general be faceted.

(iii) Bubbles can move by surface diffusion, volume diffusion or vapour transport mechanisms. There is also the possibility that the migration rate may not be diffusion controlled but interface reaction controlled.

(iv) Driving forces for bubble migration include stress gradients, moving dislocations and grain boundaries, and temperature gradients.

(v) In metals containing inert gas bubbles and subjected to an isothermal anneal the bubble size will increase by a migration and coalescence mechanism.

(vi) Experimental results for bubble migration in temperature gradients in ceramic fuel materials show that the bubbles move up the gradient by a surface diffusion mechanism, this being deduced from the radius dependence of the migration velocity. No results have been published for controlled temperature gradients in metals, but heat pulsing experiments in the electron microscope have shown a radius dependence for copper which indicates a surface diffusion mechanism.

No experimental verification of the theories of random migration and coalescence have been published. The results that have been reported show \( r \propto \sqrt{t} \) where \( n \) has a much lower value than predicted by the theory.
5. THE EXPERIMENTAL PROGRAMME

The experimental programme was concerned with two experimental techniques and two materials.

One of the most common fuel cladding materials in modern reactors is stainless steel. It was decided that as a starting point for the understanding of bubble migration through austenitic stainless steel, it would be desirable to start by looking at pure iron in the ferritic and austenitic states with the possibility of investigating the effects of the alloying additions that make up austenitic stainless steel at a later date.

The basic information required is the bubble mobility. As iron is not a convenient material for a transmission electron microscopy examination due to its ferromagnetism it was decided not to attempt a migration and coalescence type of investigation for this material. Under normal operating conditions in a reactor the cladding material is subjected to a steep temperature gradient so that migration and coalescence is probably not the most appropriate investigation. It was therefore decided to attempt a temperature gradient induced migration study for helium bubbles in both ferritic and austenitic iron, particularly as iron has one convenient property for such a study i.e. a phase change which can be used to calibrate the temperature distribution.

The other material to be studied was niobium. The primary interest in this material is as a prospective structural material for the containment vessel of a thermonuclear reactor. Here there is a severe helium production problem under the expected irradiation conditions and therefore quantitative information about the behaviour of helium bubbles in niobium is required. The radiation damage problems associated with a thermonuclear reactor have been reviewed by Martin (45). In this case it was decided to
start with a migration and coalescence type of investigation with a possible extension at a later date to temperature gradient behaviour.

Both experimental investigations were relatively original. No controlled temperature gradient investigation had been reported in the literature for a metal and no migration and coalescence study had been carried out using ion implantation as the means of introducing the helium.

The two experimental programmes will now be described in detail.

3.1 The Experimental Investigation of Helium Bubble Migration in Iron Subjected to a Temperature Gradient

3.1.1 Introduction

This programme of work was started in an industrial research laboratory (Atomic Power Construction Ltd., R & D Laboratories, Heston) and it was a requirement that the work should be carried out completely within the laboratory with no need for irradiations or implantations to be carried out in other establishments. It was therefore decided to build a small low energy accelerator for the implantation of helium into iron foils. Financial considerations limited the accelerating energy to 50 kV (sufficient for a 2000Å penetration into iron) and the machine was constructed from vacuum pumping components already available in the laboratory.

As no vacuum furnaces were available it was necessary to construct a vacuum furnace which could be used for both isothermal and temperature gradient anneals in a vacuum of about 10⁻⁶ torr, with a maximum temperature requirement for the isothermal anneals of about 1200°C (well into the austenitic region). As there was also likely to be the need for high temperature implantations in the accelerator, it was decided to use electron bombardment heating for all three functions using a 600 volt,
350mA power supply that was available in the laboratory. Electron bombardment heating is a particularly convenient technique for the heating of small specimens in vacuum. It is a convenient technique for the production of steep temperature gradients in specimens of simple geometry.

3.1.2 The Experimental Technique

Equipment needed to be constructed so that 3mm diameter iron specimens could be given the following treatments:

i) anneal at 895°C (safely below the transition temperature at 910°C) to produce a stable grain structure prior to implantation and for post-implantation annealing to produce helium bubbles.

ii) implant with 50 keV helium ions (at elevated temperatures if necessary).

iii) anneal in a temperature gradient of approximately 1000°C cm⁻¹ at temperatures between 750°C and 1200°C (average temperature over migration distance).

The next stage would be the sectioning of the specimen and the development of a suitable technique for measuring the bubble migration. Electron microscopy techniques would be preferred for this measurement as the available resolution should make it possible to measure the bubble size with a reasonable degree of accuracy. As experimental problems were to be expected, optical techniques would provide an alternative, but inferior, technique suitable only for large bubbles.

Investigations of bubble migration in a temperature gradient in uranium carbide (83), uranium dioxide (85) and copper (26) have all shown migration up the temperature gradient. Consequently the temperature gradient anneal needed to be arranged so that the bubbles migrated up the temperature
gradient and away from the implanted surface into material unaffected by radiation damage.

In order to obtain the appropriate temperature and temperature gradient at the layer of helium bubbles below the implanted surface it was necessary to form a composite specimen, so that one end could be heated and the other water cooled with the helium layer in the appropriate intermediate position for the required temperature. It was decided to achieve this by diffusion welding the implanted face of a cylindrical specimen 3mm diameter and approximately 3mm long, to a similar iron cylinder about 10 mm long. There was some concern about the prospect of creating a diffusion weld when the bubbles were so close to the implanted surface (50 keV helium ions give a penetration of about $200\mu$). Consequently it was decided to evaporate several microns of iron onto the implanted surface so that the diffusion weld bond was somewhat more remote from the layer of helium bubbles.

As there was also a danger of there being some voids along the weld line which would disturb locally the temperature gradient and which might grow and coalesce with the helium bubbles during the temperature gradient anneal, the iron deposition would tend to minimise these two problems.

The composite specimen would then be water cooled at the end formed from the longer iron cylinder and heated by electron bombardment at the end formed from the implanted cylindrical specimen so that the bubbles migrate away from the implanted surface towards the hot end of the composite specimen (assuming that the bubbles migrate up the temperature gradient).
3.1.3 The Experimental Details

The specimens were cut from 3 mm diameter rods of Johnson Matthey specpure iron. The material was not available at this diameter so that larger diameter rod had to be drawn down to 3 mm and then annealed to produce a large stable equiaxed grain structure suitable for the bubble migration studies.

Specimens were cut from this rod with lengths ranging from 3 mm to about 5 mm depending on the migration temperature required. The ends were then machined in a lathe to produce a good finish and the end to be implanted was polished. The polished specimen was then annealed for one hour at a temperature just below the $\alpha - \gamma$ phase change ($895^\circ$C) in the vacuum furnace to produce a stable structure and to recover or recrystallise out any strain that may have been introduced by the cutting and polishing.

These specimens were then implanted with 50keV helium ions, usually at an elevated temperature of up to 850°C. After implantation the specimens were transferred back to the vacuum annealing furnace and given another isothermal anneal at 895°C for one hour to produce a stable layer of helium bubbles just below the polished surface.

The next stage was to diffusion weld the implanted cylindrical specimen to another similarly prepared but longer cylindrical specimen to make up a composite specimen for the temperature gradient anneal with a length of about 13 mm. The weld was achieved by first cleaning the two polished surfaces by sputtering, then vapour depositing iron onto the implanted surface to a thickness of about a micron, and then bringing the two surfaces into contact with as high a contact pressure as was possible without seriously distorting the specimen during the diffusion weld anneal of six hours at 895°C.
The specimen was then removed from the vacuum furnace, the ends machined to a good finish to give the length and helium layer position required for the temperature gradient anneal. The end of the specimen to be at the cold end of the temperature gradient was then soft soldered to one face of a cylindrical copper block, 3\(\frac{3}{4}\)" diameter and \(\frac{1}{4}\)" thick. The resulting assembly was then ready for mounting in the temperature gradient heating assembly. The copper block was then clamped to a water cooled copper block and a thermocouple inserted into the specimen block so that the cold end temperature could be measured. The other end of the specimen was then heated by electron bombardment so that a temperature gradient in excess of 1000°C cm\(^{-1}\) was generated in the region containing the bubbles. The temperature distribution could be calculated from the power input at the hot end, thermal conductivity data and the cold end temperature, and could be checked by evidence of the position of the phase boundary (\(\alpha - \gamma\)). The temperature gradient anneal was terminated by quickly switching off the power so that the material in the phase boundary region would be subjected to a rapid cooling rate in order to make the boundary position visible by a metallographically evident discontinuity in the structure.

The specimen was then removed from the temperature gradient furnace, mounted in plastic, sectioned, mechanically polished and finally electropolished.

The bubble position was originally to be measured using a direct carbon replica for the electron microscope, but eventually differential interference contrast optical microscopy was found to be the most suitable technique.

The equipment made for this investigation will now be described in detail.
The accelerator was specifically designed for the acceleration and analysis of 50keV He\(^+\) ions. The light mass of the helium ion meant that a relatively small electromagnet could be used for the analysis of the beam. Figure (5) is a schematic diagram showing the layout of the machine and Figure (6) is a photograph of the machine.

(i) Ion Source

Figure (7) illustrates the construction of the ion source. A hot cathode Penning type source was constructed so that beam currents of approximately \(\frac{1}{2}\) mA of helium ions could be produced, the overall output being limited by the 1 mA current available from the 50 kV high voltage supply.

The body of the ion source was constructed so that the flange sealing onto the accelerator tube, the rotatable flange to which the electrical leadthrough flange was fixed and the outer jacket of the source provide the magnetic circuit for the coil, the anticathode and the filament pole being the pole pieces. This enabled a magnetic field of approximately \(\frac{1}{2}\) kG to be produced in the arc chamber. The magnet coil was completely immersed in cooling oil which is pumped from a heat exchanger at ground potential. The tube in which the arc chamber was situated was made of an austenitic (i.e. non-magnetic) stainless steel and the magnetic circuit components were made of a ferritic 12\%Cr stainless steel with the exception of the outer jacket which was made of mild steel. The austenitic and ferritic stainless steel components were joined by vacuum brazing.

The anode was made from 1\(\frac{1}{4}\)" o.d \times 26 swg stainless steel tube and the filament wound from 0.6 mm diameter tungsten wire. The filament geometry was chosen to be helical with the axis parallel to the
axis of the source so that a large fraction of the ions from the discharge attracted towards the cathode pass along the axis of the helix and do not hit the filament. This feature combined with the low sputtering rate associated with the helium ions resulted in a long filament life (in excess of 1000 hours under typical operating conditions).

The anti-cathode had a 2mm diameter and 2 mm long aperture. Helium ion currents of $\frac{1}{2}$ mA were easily extracted with an arc current of 0.25 A and an arc voltage of 150 volts.

The supplies to the ion source were housed in a cabinet above the accelerator tube. The supplies consisted of:–

a) Filament supply, 0-12 volts, 50 A A.C.

b) Arc supply, 0-250 V, 1A D.C. smoothed to $5\%$ ripple.

c) Magnet coil supply, 0-250 V, 1 A D.C. smoothed to $5\%$ ripple.

(ii) Accelerator Tube

The 50kV acceleration was achieved in a single gap at the extraction electrode. The construction of the accelerator tube is shown in Figure (8). It consists of a three electrode extraction and focussing system, the lens being of the Einzel or 'unipotential' type as described by Liebmann (187).

The extraction electrode was at ground potential, the centre electrode at the ion source voltage and the movable focus control electrode was at ground potential. The electrodes were made of stainless steel and the insulators were standard glass pipeline sections. The advantage of this system is that extraction and focusing could be achieved with a single power supply.
(iii) **Vacuum Chamber**

The ion source and accelerator tube were pumped by a single 9" diffusion pump situated under the vacuum chamber pumping through a water cooled chevron baffle. The pump was an Edwards F903B diffusion pump which was modified so that a higher heater temperature could be achieved so that an ultra-clean diffusion pump oil could be used (Convalex-10). This was achieved by lagging the bottom of the pump with insulating material.

A conduction cooled cold-cap was also added to this pump to improve the backstreaming characteristics and the base vacuum measured on an ionisation gauge was typically $7.10 \times 10^{-7}$ torr.

(iv) **Magnetic Analysis**

The function of the analysing magnet is to select the particular ion required and to make sure that the impurity ions (of different mass and therefore deflected through a different angle) do not reach the target. In this case the required ion was helium which, being a light ion, can be deflected by a small electromagnet. Also the resolution requirement for helium is not very stringent, the neighbouring elements (H, Li) having significantly different masses, and consequently a deflection angle of 20° was considered sufficient.

A simple magnet was constructed (see Figure 5) with two coils 20 cms long, 10 cms o/d wound with 18 s.w.g. enamelled copper wire. The coils were wound on copper bobbins which were water cooled. The pole pieces were 7.5 cms diameter, each with two movable 'flats' to control the focussing of the magnet in the horizontal plane (see Figure 5). The pole gap was approximately 3 cms. The flight tube that passed between these poles was an AEI- MS 10 mass spectrometer body and the beam outlet
flange had two ports, one for the straight through beam the other for the 20° analysed beam.

The magnet power supply was a 50V, 10A current stabilised power supply and magnetic fields of up to 10kG could be achieved.

(v) Target Chamber

The target chamber was constructed from standard 38 mm diameter UHV pipeline components. The layout is shown in Figure (9). At the beam entry end of the system there was an E02 2" diffusion pump with a liquid nitrogen trap and there was also a liquid nitrogen cooled cold finger baffle to minimise any hydrocarbon contamination that may come from the accelerator vacuum region.

The target position was situated at the centre of a 6-way cross-piece. The target region geometry is shown in Figure (10). The target (a 3mm diameter cylinder or foil specimen) was loaded onto a holder and the holder was then pushed into the heater assembly. This was done using a vacuum lock which enabled part of the heater assembly to be pushed through an 'O' ring sealed aperture, so that the specimen could be loaded into the target chamber without destroying the vacuum in the target region. When loaded, the vacuum lock flange was replaced, the vacuum lock pumped down with a rotary pump (the large rotary pump backing the 9" diffusion pump was used for this purpose) and then the target holder was pulled into the vacuum system. The rod on which this assembly was mounted passed through a double 'O' ring seal with a large volume pumped interspace so that programmed oscillation of the target angle to the beam could be carried out during implantation.

The length between these two shaft seals was chosen so that grease on the 'O' ring at the interspace/atmosphere end of the system would not be carried to the clean 'O' ring when the target holder was
pushed into the vacuum lock. This programmed oscillation, as discussed by Worth (186), was achieved with a cam mechanism, and was designed to achieve a uniform implant from \( \frac{1}{4} \) maximum depth to the maximum penetration depth. This facility was incorporated for foil implants; it was not required for the temperature gradient work.

A range of target holders were used, according to the requirement. The standard holder for elevated temperature implants of specimens for the temperature gradient work could take 4 specimens, and each specimen was brought into the beam by turning the holder shaft through 90°. Larger holders using the linear motion as well as the rotational motion could be used for low temperature implants (\( < 300^\circ C \)), and these were used for some of the early exploratory work on niobium foils.

The implantation region (see Figure 10) consisted of a cylindrical electron suppression electrode (150 volts negative) which also acted as a heat shield, a beam defining electrode at ground potential and a tungsten filament which heated the target by radiation for low temperatures (\( < 500^\circ C \)) and by electron bombardment for temperatures from 500°C to 1200°C. The beam defining electrode determines the diameter of the beam hitting the target and prevents the beam from hitting the electron suppression electrode as this would produce secondary electrons that would stream back to the target giving an incorrect ion beam current measurement. The electron suppression electrode was necessary to prevent secondary electrons from escaping from the target during bombardment so that an accurate ion beam current measurement could be obtained. The tungsten filament electron bombardment heater heated a hollow cylindrical block surrounding the target block and electrically insulated from it. The heat was transferred by radiation and by conduction through the alumina insulators. This enabled
the ion current to be measured while the electron bombardment heater was being used.

When an elevated temperature implant had been completed, the specimen holder was pushed into a copper cooling block so that the assembly could be cooled down to 100°C before pushing the holder into the vacuum lock. This was found necessary as the target was thermally well isolated and cooling below 400°C was extremely slow.

An on/off type temperature controller was used to switch the electron bombardment voltage using a relay with mercury contacts. A 1/16" diameter sheathed Cromel/Alumel thermocouple measured the temperature and the ion current was collected on the sheath of this thermocouple.

vi) Performance of the Accelerator

1/4mA beams of 50keV helium ions were easily achieved, and the beam size at the target could be varied from a 1mm diameter spot to a parallel flood beam occupying most of the diameter of the flight tube. The beam was usually used in this latter condition because typically currents of about 10μA were required and the defocussing was used to produce a uniform current density (approximately ± 5% uniformity) over the 3mm diameter area of the specimen. The beam defining aperture limited the beam diameter at the target to 5mm diameter.

The beam current was measured on a 25μA full scale moving coil meter and the beam current would be stable to better than 5% during a typical implant of about 5 minutes.

3.1.5 The Vacuum Furnace

The vacuum furnace system was required to perform three functions:

a) Isothermal anneals for structure stabilisation and helium bubble
production and growth, and this was carried out at 895°C.

b) diffusion weld anneals - also carried out at 895°C.

c) temperature gradient anneals.

The layout of the vacuum furnace is shown in Figure(11). The upper part of the vacuum vessel contained the electron bombardment heated iron crucible in which the isothermal anneals were carried out. The bottom of this crucible was covered with a fine layer of alumina particles sintered into the surface of the crucible to prevent the specimens diffusion welding to the crucible, this being critically important during the diffusion weld anneals. The position of the thermocouple possibly gave a slightly high temperature compared with the specimen temperature as it was close to the heat generation region, but this was desirable because it is important that the specimens did not go into the γ-phase, partly because of the lower diffusion constant, but also because the phase boundary might drag the bubbles along with it.

For the diffusion weld anneal, the lower long cylinder (approximately 10mm long) and the implanted specimen were aligned with a split tube jig and the 6BA stainless steel screw tightened down onto a dimple machined on the rear face of the implanted specimen. The screw support system had quite a lot of intrinsic elasticity (i.e. not too rigid) and the pressure on the specimen could be adjusted quite precisely.

The temperature gradient anneals were performed in the lower part of the vacuum vessel. The iron specimen/copper block composite specimen was clamped rigidly to a water cooled copper block so that there was good thermal contact. A thermocouple was then inserted into the specimen block so that the cool end temperature could be measured.
The top of the specimen was heated by electron bombardment. Originally a 3mm diameter oxide coated klystron cathode was used but these were not reliable. It is suspected that the burst of gas from the specimen surface during the initial heating was poisoning the cathode. Consequently a helical tungsten wire cathode was used, wound from 0.3mm diameter tungsten wire (see Figure 12). The top of the 3mm diameter specimen was level with the top surface of a plate with a 4mm diameter hole in it in which the specimen was situated. This plate and every surface in line of sight with the filament was at filament potential, so that the top surface of the specimen was the only anodic surface available to the electrons. The strong field down the 3mm wide gap between the sides of the specimen and the plate would prevent any significant tendency for bombardment along the side surfaces of the specimen. The relatively large filament spiral diameter was used to minimise the tendency for the bombardment heating to be too localised at the centre of the top face of the specimen.

The 600 volt supply used for the other heating requirements was not found to be suitable for the temperature gradient heating, as space charge was limiting the bombardment current to too low a value. Consequently a 1500V supply was used. Initially this was an unstabilised supply and stability against drift had to be achieved by laborious manual adjustment. Eventually this was replaced by a power stabilised supply (i.e. product voltage x current was stabilised) with a digital read-out of power input into the specimen, in the range 20.0 to 30.0 watts.

The system was pumped by a 2" diffusion pump, using Convalex 10 diffusion pump oil, and the ultimate vacuum was in the 10^{-7} torr range.
The Sputter Cleaning and Iron Deposition Apparatus

The layout of this system is shown in Figure (13), and was designed to fit into a standard Edwards evaporator vacuum system (12" Bell-jar type). This enabled the specimens to be sputter cleaned using an argon glow discharge followed immediately by evaporation of iron from a multi-strand tungsten filament. The cleaning and evaporation process was not started until the vacuum was well into the 10^-7 torr range. The standard equipment supplied with the evaporator was not suitable for this work, mainly because the sputtering intensity available was found to be too low to clean the iron specimens effectively. The success of this vapour deposition process was found to be critically dependent upon this sputter cleaning stage carried out before the vapour deposition.

The Polishing Technique

It was an essential requirement of the diffusion weld technique for producing the temperature gradient specimens that the polished surfaces were extremely well polished and flat.

This was achieved by mounting up to 32 specimens in an iron block approximately 10 cms square and 5 cms thick.

The specimens were each held in position by a 10BA screw and when completely loaded the block together with its specimens was skimmed flat on a surface grinder, using a fine grade grinding wheel.

The block was then transferred to an ultrasonic polishing machine and was given overnight polishing runs with 6, 1, and 1/10 micron diamond polishing compound. After polishing the specimens were removed, ultrasonically cleaned in alcohol and then stored in a dessicator.
3.2 The Experimental Investigation of the Migration and Coalescence of Helium Bubbles in Niobium

3.2.1 Introduction

There did not appear to have been any investigations of inert gas bubble migration and coalescence reported in the literature for materials where the inert gas had been introduced by ion implantation. This was primarily due to two important factors:

i) migration and coalescence studies require that the helium containing material should be reasonably thick so that the bubble interaction is 3-dimensional. A thin 2-dimensional layer of implanted helium does not reproduce the conditions found in reactors and creates a difficult situation from the analysis point of view and requires precise knowledge of the distribution.

ii) the need for a wide band of implanted helium, preferably not too close to the surface requires the development of techniques for stripping a precisely controlled amount of material from the surface before preparing the thin foil for transmission electron microscopy. Also the technique for producing the thin foil must not unintentionally remove helium containing material; the foil must be produced by thinning from one side and there must be no chemical attack of the side containing the implanted helium.

For this investigation, a near uniform concentration of helium was produced in niobium in an estimated depth range from 2100Å to 8500Å by ion implantation at four different energies. The surface layers were then removed by anodic oxidation and thin foils prepared for transmission electron microscopical examination of the helium bubble behaviour as a function of annealing temperature, annealing time and helium concentration.
The advantages of helium ion implantation are that there is relatively little radiation damage caused by the implant, it is inexpensive compared with neutron irradiation, there is no need for alloying additives to give the required \((n, \alpha)\) reactions and the bubble mobility is not complicated by fission product impurities, which have been shown to influence bubble mobility (79) (169).

3.2.2 The Experimental Programme

The primary aim of this work was to investigate the relationship between bubble size and density as a function of annealing temperature and duration, for temperatures in the range 850°C - 1450°C and durations up to 100 hours. A short preliminary investigation of the effect of helium concentration was carried out for a one hour anneal at 1250°C.

Specimens 22 mm x 15 mm were cut from 0.002" Nb sheet, chemically cleaned and then given a stabilising pre-irradiation anneal. Implantation was carried out to produce an approximately uniform implant from 2100Å to 8500Å penetration. The specimens were then given a range of post irradiation anneals. The specimens were then given an anodising treatment to remove, for the initial programme, a nominal 3000Å - 5000Å of niobium so that foils could be prepared to investigate the bubble size from this depth through the thickness of the foil, which in general would be about 1500Å.

The experimental techniques used will now be described in detail.

3.2.3 The Ion Implantation

The ion implantation programme for this work was divided into two categories:

i) single low energy implants (50keV) using the small accelerator described earlier.

ii) higher energy implants at four different energies for the
quantitative work. These implants were carried out on the 600kV machine in the Electrical Engineering Department of the University of Surrey (190).

The 50kV machine was used basically for testing the techniques used for anodizing and stripping surface layers from the helium implanted niobium and for the electropolishing of foils for the transmission electron microscope. This was particularly necessary as the anodizing technique was affected by the presence of the helium bubbles and the electropolishing using conventional techniques invariably resulted in the helium containing material near to the electron transparent areas of the foil being removed or partly removed so that quantitative work was not possible. The dose rate for the 50kV machine was typically 60μA cm⁻².

The higher energy implants were carried out at four energies, 220, 140, 100 and 50 keV in order of decreasing energy at a dose rate of 10μA cm⁻². The relative doses were selected so that the calculated concentrations at the penetration depths for the four energies were equal. This resulted in a calculated distribution constant to within ± 6% from 2100Å - 8500Å and ± 1% from 3500Å - 6500Å and this distribution is shown in Figure (14). The range information was obtained from a computer programme based on the results of Linhard et al (191).

3.2.4 Heat Treatment

i) Pre-irradiation Heat Treatment

A pre-irradiation heat treatment of 1350°C/1 hour was found necessary to ensure that the structure was stable and to prevent any possibility of recrystallisation during subsequent post-irradiation annealing.

As the vacuum furnace was only capable of a vacuum of the order of 5 x 10⁻⁶ torr and niobium is capable of picking up significant quantities of oxygen and nitrogen, which may have a significant effect on the bubble migration properties, the specimen crucible and the region above it were
lined with zirconium sheet acting as a getter (192). This was arranged so that all surfaces in line of sight with the niobium were zirconium, with the exception of the tungsten wire used to support the specimens. Hardness checks are a sensitive means for detecting oxygen and/or nitrogen pick up in niobium (193) (194) and microhardness measurements were made on specimens after a variety of heat treatments.

ii) Post-irradiation Heat Treatment

The post-irradiation anneals were carried out at temperatures from 850°C to 1450°C for durations ranging from 1/2 hour to 100 hours. The heating and cooling times for this furnace did not allow shorter anneals than 1/2 hour.

3.2.5 The Anodising Technique

The technique used was based on that used previously for the analysis of diffusion specimens by Pawel and Lundy (195).

The anodising solution was 0.5% Na₂SO₄ in distilled water with 2 drops of HF per 100 ml added to facilitate the stripping of the oxide film. The solution was used originally without stirring at 20°C and a fresh solution was made up each day. The anodising was initially carried out at a constant current density of 2.5 mA cm⁻² with a stainless steel cathode, and observation of the increase in voltage across the cell during the anodising process indicated that anodising occurred smoothly and linearly with time up to a voltage of about 200 volts when behaviour became erratic due to breakdown. The electrical connection was made to the specimen with a crocodile clip and the clip and the surfaces not to be anodised were coated with 'lacconit' laquer so that a 15 mm square area at one end and one side of the 22 mm x 15 mm specimen was available for anodising. The edges were also coated as this was found to be a likely region for premature breakdown.
The stripping was originally carried out using a cellulose acetate film 'wetted' with acetone. This was placed on the anodised specimen, the lacquer having previously been dissolved off with acetone, and allowed to dry. Then the film was pulled off, bringing the anodic film with it.

Originally it had been hoped that it would be possible to pre-calibrate the amount of niobium removed by anodising the niobium and stripping off the oxide film. But it was found that the weight gain on anodising and the weight loss after stripping varied from specimen to specimen, and particularly varied for the repeated stripping of one specimen, the second stripping invariably producing the largest weight loss. Another problem was the reliability of the process, which decreased with the progressive stripping of one specimen. The following variables were considered:

- a) current density for the anodising process.
- b) electrolyte temperature
- c) electrolyte stirring
- d) electrolyte composition
- e) cathode polarisation
- f) surface finish of the niobium
- g) annealing treatment.

It appeared likely that recrystallisation of the anodic oxide film was one major contribution to the formation of irregular films which were difficult to strip. There is evidence (196) to suggest that a high current density (i.e. a rapid rate of film formation) and also probably a low temperature would decrease the probability of recrystallisation. It was in fact found that a current density of 10mA cm$^{-2}$ with a stirred and cooled (0°C) electrolyte greatly improved the reliability of the process, particularly for the progressive stripping of one specimen. When lower current densities e.g. 1mA cm$^{-2}$ were used with the electrolyte at 20°C the
second anodised film invariably had a patchy interference colour and was always difficult to strip.

The problem of variable niobium removal for apparently fixed experimental conditions was not resolved, and it was concluded that weight measurements should be taken after each operation.

The amount of niobium anodised was also affected by the presence of helium bubbles but, more seriously, the stripping operation became extremely difficult so that eventually it was decided that the film would have to be dissolved off.

The anodised film was dissolved off using a 10\% HF in H_2SO_4 solution at about 35°C. The main problem was the difficulty of determining accurately when the oxide has been removed as the solution was found to dissolve the metal at a rather unpredictable rate. Following the change in interference colours allowed an estimate of the necessary time to be made, but this was not considered to be sufficiently accurate. The problem was overcome by applying a 1\frac{1}{2} volt negative potential to the specimen, using a platinum anode, and this was found to prevent the metal from dissolving without preventing the solution of the oxide. A higher voltage prevented the oxide from dissolving as well.

3.2.6 Foil Preparation

Conventional foil preparation techniques based on the 'window' (197) and 'PTFE holder' (198) techniques for back-thinning with the implanted face protected with a laquer did not give sufficiently reliable results for a quantitative investigation. In the majority of foils prepared by these techniques helium bubbles were either absent or insufficient to account for the implanted concentration. After extensive experimentation with different variations of these techniques using different protective materials and also
using photocell operated switching to remove the electropolishing voltage as soon as perforation occurred, it was decided that a fundamentally different technique was required.

A suitable technique was developed and is described in detail in Appendix I. The technique relies on a heavy organic liquid which protects the implanted face of the specimen (facing downwards) and which is held at a positive pressure with respect to the electrolyte (above the specimen). When the perforation reaches a critical diameter, the organic liquid flows through and covers the top of the specimen, thus isolating it from the electrolyte both chemically and electrically. The success of this technique is probably predominantly due to the chemical isolation given by this technique, as the electrolyte attacks the niobium significantly with no applied voltage.

3.2.7 Electron Microscopy

The bubble size and distribution was investigated by transmission electron microscopy using a JEM-100B microscope.

A tilting stage was used to get the best diffraction conditions and the photographs were taken with the bubbles slightly out of focus for good bubble contrast but not sufficiently out of focus to give a significant measurement error.

3.2.8 Bubble Measurement

The best technique for the measurement of bubble sizes was found to be the measurement, with a ruler, in \( \frac{1}{2} \) mm units from enlarged prints (up to 7x plate size). Measurements direct from the plates or from small prints using magnifying measuring devices was not found suitable, particularly when the bubbles were poorly contrasted.

The number of measurements taken from each bubble depended on the shape of the bubble profile, as the bubbles in niobium were invariably sharply
faceted. Generally three measurements were taken, between opposite facets if the orientation was such that a hexagonal profile was produced or two measurements for (100) micrographs where the profile was square or rectangular. For intermediate orientations three measurements were usually taken, the measuring directions being the same for all the bubbles in the photograph.
4. RESULTS

4.1 Temperature Gradient in Iron

4.1.1 Helium Bubble Production

The initial requirement was to find the conditions necessary to produce a suitable distribution of bubbles, which for a 50keV implantation energy will be approximately 2000Å below the surface.

As the major experimental difficulty was likely to be the development of a suitable technique for detecting the position of bubbles after the temperature gradient anneal, it was decided that the initial experiments should concentrate on relatively large bubbles (approximately 1000Å radius) which, it was hoped, would be relatively easy to see on a direct carbon replica taken from an electropolished axial section of the specimen.

Unfortunately there were many problems associated with looking at the line of bubbles in an axial section, particularly when many of the bubbles had not migrated away from the implanted surface, and these are discussed in the next section. Consequently it was decided that the best technique for evaluating the implantation conditions would be to observe the implanted surface after annealing, using a scanning electron microscope and to estimate the size of the bubbles as they break the surface. It would not be desirable for the bubbles to be in contact with the surface as the specimen/evaporated iron interface would probably restrain the movement of the bubbles in the temperature gradient. So it was therefore necessary to find implantation conditions such that after prolonged anneals at 895°C (6 hours) no more than a minor fraction of the bubbles reached the surface, but the bubble size needed to be reasonably large (say 1000Å.
radius).

To get an idea of the dose required, the amount of helium required to produce a monolayer of close packed bubbles on a square lattice was calculated. Assuming the ideal gas laws are obeyed, this dose works out to be independent of bubble radius, the value being $2 \frac{Y}{kT} \pi \text{ ions cm}^{-2}$. Taking $Y$ for $\alpha$-iron as 1950 ergs cm$^{-2}$, the value found by Price et al. (199) for $\delta$-Fe, this evaluates to $2.5 \times 10^{16}$ ions cm$^{-2}$.

Implantation at this dose at room temperature followed by a 6 hour anneal at $895^\circ C$ produced no detectable bubble evolution at the surface. If bubbles had been evolved they were either small compared with the resolution of the scanning electron microscope (say 250Å) or the surface craters healed very quickly. Increasing the dose to $7.5 \times 10^{17}$ ions cm$^{-2}$ caused blistering of the surface as shown in Figure (15). A similar phenomenon has been reported by Erents and McCracken (200) after high dose helium ion bombardment of molybdenum. No intermediate dose was found that produced bubble evolution upon annealing that did not produce blistering during implantation.

The fact that room temperature implantation did not produce large bubbles ($\sim 1000$Å radius) had been anticipated and a hot target facility for the accelerator had been constructed.

As there was some concern that an elevated temperature implant might result in a nucleation problem with the implanted atoms drifting away from the implanted surface without being trapped in bubbles, it was decided to implant initially at room temperature followed by the high temperature implant. The result of such an implant, $10^{16}$ ions cm$^{-2}$ at room temperature followed by $2 \times 10^{16}$ ions cm$^{-2}$ at $600^\circ C$ is shown in Figure (16). The larger blisters in this stereoscan micrograph are between
1000 - 1500Å radius. This particular micrograph is of a specimen which has been given a 10 minute anneal at 895°C, but it was found that the result was not particularly sensitive to annealing time, indicating that most of the blisters have been produced during the implant rather than during the anneal. It is noticeable that very few blisters have burst in Figure (16) whereas for example specimen given $10^{15}$ ions cm$^{-2}$ at room temperature and $4 \times 10^{16}$ ions cm$^{-2}$ at 850°C (Figure 17) has many holes in the surface (4000 - 6000Å diameter) and considerable debris resulting from burst blisters. This is to be expected as the radius of the bubble is commensurate with the penetration depth of the ions.

The conditions selected as most suitable for the initial temperature gradient experiments was $0.5 \times 10^{16}$ ions cm$^{-2}$ at room temperature followed by $1.5 \times 10^{16}$ ions cm$^{-2}$ at 600°C. After a one hour anneal at 895°C the number of bubble blisters on the surface was rather lower than in Figure (16) ($3 \times 10^{16}$ ions cm$^{-2}$) and the bubbles were marginally smaller averaging about 2000Å blister diameter. Under these conditions the only blisters to burst at the surface were those from bubbles at grain boundaries where the bubble size was somewhat larger.

4.1.2 Observation of Bubble Movement

One of the major experimental difficulties was to find a technique suitable for looking at the position of the band of helium bubbles in a plane through the axis of the cylindrical specimen.

Transmission electron microscopy was not practical for three reasons:

a) the iron is ferromagnetic - this makes electron microscopy difficult. Foils were produced from thin iron foil (about 0.002" thick),
but the astigmatism produced by the ferromagnetism made transmission microscopy difficult, even with demagnetised specimens.

b) if transmission electron microscopy of a ferromagnetic material is to be considered for measuring bubble migration then low mass foils must be produced with the specimen axis parallel to the plane of the foil.

c) even if the above is achieved, the foil perforation (i.e. the electron transparent material) must be in the appropriate position.

Consequently this technique was not actively pursued.

The direct carbon replica technique \(^{(201)}\) proved to be no less difficult. A considerable period of time was devoted to attempting to remove carbon films from either electropolished or sputter etched sections. Unfortunately there was invariably a row of bubbles or voids along the diffusion weld line and this acted as a line of weakness for the carbon film. Consequently films either floated off in many pieces or tore along the diffusion weld line during the removal process. Eventually after extensive experimentation with different stripping techniques, the technique had to be abandoned.

During the attempts to produce carbon replicas it became evident that another major problem was the production of artifacts produced by the electropolishing which at high magnifications made it difficult to differentiate between bubbles and artifacts. Sputter etching was tedious and problems developed due to the heating of the plastic mount.

At this stage it was decided to restrict the investigation to large bubbles, to give long temperature gradient anneals so that substantial migrations occurred (i.e. tens of microns) so that observations and measurements could be carried out using either the scanning electron microscope or optical microscopy. Although the bubble size would apparently be too small for optical microscopy, one of the intrinsic disadvantages of electropolishing and normal sputter etching (i.e. ion bombardment perpendicular
to the surface) for bubble measurement i.e. the enlargement of the apparent bubble size can here be utilised (see Figure 18). This, in fact, was the technique used, and the use of differential interference contrast increases the ability to detect the shallow depression resulting from electropolishing through a bubble. One of the major disadvantages found with the use of the scanning electron microscope was the poor resolution and contrast when used at low magnification, and when dealing with a band of bubbles migrating away from a surface a low magnification is desirable so that the line of bubbles can be differentiated from artifacts and the measurement of the migration distance made.

4.1.3 Temperature Gradient Calibration

One advantage of iron as a material for a temperature gradient study is that the phase change which will be in a stationary position in the specimen during the anneal should give a calibration of the position of the temperature of the phase change. For this reason the power was always removed quickly by switching the electron bombardment voltage and filament current off together at the end of a temperature gradient anneal. The cooling rate, estimated from graphical information from Carslaw and Jaeger (163), for the iron in the γ phase close to the phase change boundary when that boundary is 10 mm from the cold end in a 13 mm long specimen is in excess of 100°C sec⁻¹ in the range down to about 500°C. This would be expected to produce a discontinuity, with fine ferrite grains resulting from the rapid transformation from the austenitic phase. On the ferrite side of this boundary, the large grains of the stabilised ferrite structure would remain resulting in a distinct discontinuity in grain size. Such an effect is shown in Figure (19), a calibration specimen with no weld, subjected to a 26 watt power input (approximately 400 watts cm⁻²).
Figure (20) shows the thermal conductivity information as a function of temperature plotted out, the information coming from two sources (202) (203). From this information the temperature distribution and therefore the position of the phase change boundary and the temperature and temperature gradient at the helium bubble position can be calculated. Figure (21) shows a plot of temperature at a position 10mm from the cold end and the temperature gradient in material above the Curie temperature (768°C) as a function of electron bombardment power. The power level calculated from the observed position of the phase change boundary using the thermal conductivity data and the measured power input never varied significantly more than 0.25 watts, and this can give some idea of the accuracy with which the temperature distribution can be estimated i.e. to within ±13°C.

Initially it had been expected that the phase change boundary would be visible in all specimens, so that each temperature gradient anneal had its own temperature calibration. Unfortunately when the boundary was close to the diffusion weld and on the high temperature side of it, the weld line appeared to interfere with the grain growth in the α-iron, and the phase change position was not evident.

The time taken to achieve a stable temperature distribution at the beginning of the anneal was estimated from equations from Carslaw and Jaeger (163) and were of the order of ½ minute. Test durations were 6 hours.

4.1.4 Bubble Migration Results

A total of 19 temperature gradient anneals were carried out, the first 8 with an unstabilised supply where the constant power input into the specimen had to be maintained by manual adjustment (specimens
TGI - TG8) and then 11 specimens with the constant power electron bombardment supply (STGI - STG11).

Unfortunately, out of these 19 specimens, only three, TG5, TG6 and TG8, produced a visible migration of the bubbles, TG5 and TG6 in the ferrite phase and TG8 in the austenite phase. The results, with the relevant parameters are given in Table (2).

Micrographs of these three results are given in Figures (22), (23) and (24).

It is suspected that the main reason for the high failure rate was probably the interaction of the bubbles with the implanted surface. There were in all specimens a significant number of bubbles (or voids) along the implanted surface - evaporated iron interface. There are many ways in which this could have happened:

1) The bubbles were large in diameter (approximately $1000\AA$ radius) and close to the implanted surface (approximately $2000\AA$ penetration for 50keV helium ions). Any variable which may affect either of these two quantities could have a critical effect on the proportion of bubbles which remain free from interaction with the surface. For example, if the surface cleaning by sputtering was carried out for a sufficiently long time to not only remove the oxide layer on the implanted surface but also to remove a substantial amount of iron, which has a sputtering rate thirty times as great as that for the oxide, then there could be a serious increase in the amount of bubble - surface interaction. This interaction problem had resulted from the need to change the experimental philosophy which had originally been intended to be the measurement over quite small migration distances of relatively small bubbles (about $200 - 400\AA$ radius) using electron microscopy replica techniques. The need to increase the bubble
size thus reduced the distance between the bubble surface and the implanted surface.

ii) There is a possibility that voids grew on the implanted surface—evaporated iron interface during the temperature gradient anneal. The temperature gradient produces a vacancy flow and if this interface acts as a sink but not a source for vacancies then void growth would be expected. This problem has been reported for thermal diffusion experiments (147) where voids grow either at the weld interface or at the marker/matrix interface. If these voids grow at a sufficient rate then they may coalesce with the bubbles to produce immobile voids.

iii) The stresses and strains produced during the diffusion weld may have caused the bubbles to move towards the implanted surface. It is a difficult process to reproduce with a consistent amount of deformation and may therefore have been the main cause of the inconsistency in achieving bubble migration. Unfortunately a high contact pressure was necessary in order to ensure that a good void free weld was obtained.

iv) The evaporation of iron onto the implanted surface produces an evaporated layer with a high tensile stress. Considerable difficulty was experienced initially with the evaporation of iron films onto the iron surface as there was a tendency for the film to rupture and flake off. This suggested both poor adhesion and high stresses. This phenomenon has been reported by several authors (204) (205) (206). It was cured by evaporating onto the surface at an elevated temperature (approximately 200°C) and by thorough surface cleaning by sputtering immediately before vapour deposition. Although this prevented the rupturing of the vapour deposited iron film, it did not necessarily completely remove the stress. This stress would attract the bubbles to the surface (57) (58).
This effect would not occur if the surface was completely oxide free as epitaxial deposition would then be expected. It had been the intention to use sputter cleaning to remove this oxide but unfortunately the sputtering rate for the oxide is a factor of 30 lower than that for the metal. The sputter cleaning duration that would be necessary to ensure that all the oxide had been removed may therefore remove a substantial layer of metal if the oxide thickness has been overestimated. Consequently a rather shorter cleaning period was chosen which produced a clean but not oxide free surface.

With the available equipment very little could be done to reduce the contribution to experimental failure from any of the above mentioned causes. Reducing the bubble size by decreasing the dose or implantation temperature did not produce visible migrations. This could be due to the difficulty of seeing the bubbles using an optical technique. It is more likely that the higher mobility of smaller bubbles just increased the chance of interaction forces causing the migration of the bubbles to the interface.

The estimation of the force necessary to drag the bubbles away from this interface is a similar problem to that of a bubble on a grain boundary (52), where removal of the bubble radius $r$ creates an area $\pi r^2$ of new interface surface. This implies very approximately that a force $F \approx \frac{\gamma \cdot \pi r^2}{\pi r} \approx \gamma r$ is required, where $\gamma$ is the interface energy. Unlike the grain boundary case the interface being considered here is likely to be between dissimilar materials (i.e. iron and iron oxide) and the interface energy will probably have a relatively high value with the consequence that the bubble will stay at the interface and not migrate up the temperature gradient.
4.2 Results for Isothermal Annealing of Helium Bubbles in Niobium

4.2.1 Microhardness Tests

Microhardness tests were carried out to establish that no significant pick-up of oxygen or nitrogen was occurring during the annealing treatment. The microhardness results are given in Table (3). Each result in this table is the average of 6 readings, the scatter in these readings being quite severe for the 25 gm load but rather more acceptable for the 50 gm load. Higher loads were not used as the foil is only 50 microns thick. There are inconsistencies in the table, particularly between the 25 gm and 50 gm hardness results, but the results from specimens H27 and H28 reveal no objection to an annealing treatment of 1350°C/1 hour. The non-recrystallised specimen H2 has a similar hardness to H1 suggesting that the specimen had received the correct anneal. It is concluded that 1250°C/1 hour is not a sufficient pre-irradiation anneal to guarantee a stable recrystallised structure and that 1350°C/1 hour would seem appropriate, there being no evidence that this higher temperature leads to oxygen or nitrogen pick up.

4.2.2 Average Bubble Size

The results are shown in Figure (26) where bubble radius is shown as a function of annealing temperature and duration. The results are also given in Table (4). It can be seen that the results plotted on a logr/logt plot fall on straight lines with a slope of approximately 1/5, although there does seem to be a tendency towards decreased slope for bubbles with a radius larger than 100 μ.

This slope of 1/5 indicates that the bubbles migrate by a surface diffusion mechanism. If either volume diffusion or vapour transport mechanisms were operative then slopes of 4 would be expected.
The temperature dependence of the average bubble size for 1 hour anneals is given in Figure (27), where \( \log r \) is plotted against \( 1/T^0K \). The 1350°C result is excluded from this plot as the anodising treatment removed more niobium than intended and the foil has therefore been taken from a region of reduced helium concentration. To obtain an estimate of activation energy for surface diffusion \( Q_s \), \( \log r \cdot T^{-1/5} \) is plotted against \( 1/T \). From the slope of this plot, an activation energy of 81 k cals mole\(^{-1}\) is obtained, but this is based on equations which assume ideal gas behaviour in the bubbles. If the activation energy is calculated from the regression lines through the 950, 1050 and 1250°C results, calculating the activation energy from intercepts at various durations, values of \( Q_s \) from 68 to 75 k cals mole\(^{-1}\) are obtained. This will be discussed in greater detail in a later section.

Typical micrographs from which the bubble measurements are taken are shown in Figure (28).

4.2.3 Helium Concentration

The bubble sizes obtained at four helium concentrations after heat treating at 1250°C/1 hour are given in Table (5).

The highest concentration specimen has an unexpectedly low average bubble size. This may be a channelling effect (discussed in a later section) but unfortunately no more foils were available from this specimen, so this could not be checked. The results are compared in Table (5) with the \( m^{1/5} \) (m-helium concentration) dependence predicted by theoretical analyses (see equation (28)).

4.2.4 Bubble Size Distribution

Initially the bubble size measurements were aimed at calculating
an average bubble size for the distribution and measurements were taken, in $\frac{1}{2}$ mm units, from prints with an overall magnifications typically in the range 200K - 500K. At the higher magnifications and particularly for specimens annealed at a low temperature for a short duration, it was evident that the distribution was not the simple skew distribution predicted by Gruber (66) and Baroody (166). The regular presence of more than one peak in the distribution suggested that the effect was real and not just statistical scatter. Consequently some of the bubble measurements were taken from large prints (14" x 12") at higher magnifications so that a smaller measuring interval could be used in order to increase the resolution of the measurements. It was found to be more satisfactory to measure from larger prints than to magnify smaller prints or plates. The problem with decreasing the measuring interval is that the number of measurements required to give statistically significant populations in each band of the histogram also increases proportionally, and a compromise has to be reached to avoid counting an excessive number of bubbles.

The distributions obtained for 950°C anneals are given in Figure (29). Figures (30) and (31) show distributions at 1050°C and 1250°C for specimens where the measuring interval used was small enough to reveal the distribution. Unfortunately comparison is complicated by the different magnifications and measuring intervals used. A complex distribution will simplify to a simple skew distribution if the measuring interval is increased sufficiently. The magnifications and measuring intervals for most of the specimens were selected at a time when only the average size was of interest and the magnification was arbitrarily chosen to give a nominal 50 bubbles to count on each plate.

Figure (32) shows some of the results where two prints were taken from different areas of the same plate and this shows that although the distributions are usually similar there is often a displacement between
the two distributions. This suggests that dimensional changes in the photographic print may be a source of error.

4.2.5 Effect of Grain Orientation

One concern in this type of investigation was that a significant number of grains would not have the intended helium concentration because of increased ion penetration due to channelling. It was therefore necessary to get some idea of the channelling probability for ions implanted normally to the niobium sheet surface.

For this investigation a specimen was implanted with $10^{17}$ ions cm$^{-2}$ at a single energy of 100keV energy and then heat treated at 1150°C/1 hour. The surface layers were then progressively removed by anodising and chemical stripping and the surface examined by optical microscopy. When the surface after anodising passes through a region of high bubble concentration, the resulting surface profile will be irregular and will therefore appear dark in an optical microscope due to light scattering. The micrograph in Figure (33) was taken with 4400Å removed by anodising and stripping and the calculated penetration was 4100Å. The photograph indicates that there is quite a high probability of not finding the expected bubble concentration and that many grains or foils should be looked at in order to find the highest bubble concentration, as the higher penetration of channelled ions would result in a lower concentration of helium than expected in the depth range studied for this investigation (i.e. 3000 - 6000Å).

Figure (34) shows the same area with 7500Å of niobium removed from the surface, and many of the grains that were white in Figure (34a) are now darker due to the channelled ions.
4.2.6 Effect of Material Variables

Two batches of niobium were used. No attempt was made to specifically investigate differences between the two batches, but no difference is evident from the results. Specimens H1 - H35 were taken from one batch of material, the remaining specimens from the second batch.

4.2.7 General Observations

The direct measurement of bubble densities to a useful accuracy did not prove a practical proposition. When the foil surface passes through a bubble, the outline becomes blurred and the bubble is often surrounded by a ring. It was hoped that these could be used as surface markers for foil thickness measurement using stereomicroscopy but the variation in thickness of the foil from one area to another makes the application of this technique laborious and inaccurate. The 'rings' round some of these surface bubbles may be due to the helium escaping to form a bubble in the electrolyte during electropolishing. An alternative explanation is that it is caused by the enlargement of the bubble after perforation, as discussed with regard to the electropolishing of iron earlier. Figure (35) shows a micrograph with (100) orientation showing bubbles with a rectangular profile. The 'rings' round the bubbles which have intercepted the surface are also rectangular. This makes the latter explanation the most likely.

The faceting of the bubbles consists of (110) planes with some minor development of (100) planes.

The behaviour of helium bubbles in niobium grain boundaries seems to be similar to that in the grains, the bubble size and density showing no significant deviations from bulk behaviour. This suggests that under the annealing conditions given there are no lack of vacancies for bubble
growth. It is under conditions of insufficient vacancy availability that preferential growth occurs near the grain boundaries. The lack of any evidence of lenticular shaped bubbles forming on the grain boundaries suggests that the grain boundary energy is not particularly high.
5.1 Discussion of Temperature Gradient Results for Iron

The three results obtained are plotted in Figure (25) together with various theoretical estimates of the migration rate. In this plot the temperature gradients, slightly different for each specimen, have been normalised to $1000^\circ C^{-1}$ on the assumption that the migration distance is directly proportional to the temperature gradient. The surface diffusion estimates use equation (22) with $\beta_s = 3/2$ and the surface diffusion data of Matsumura (91), Blakely and Mykura (92) and Zahn (93). The value for $Q_s^*$ has arbitrarily been taken to be equal to $Q_s^*$, the activation energy for surface self-diffusion and the bubble radius has been taken to be $1000^\circ$. As the migration velocity $\propto r^{-1}$ for surface diffusion, the effect of bubble radius on these results is easily seen. The volume diffusion mechanism estimates are given using equation (23), with $\beta = 1$ and $Q_v^* = Q_v$ the diffusion information coming from Smithells (203) ($D_0 = 1.9 \text{ cm}^2 \text{ sec}^{-1}$, $Q = 57.2 \text{ k cal mole}^{-1}$ for $\alpha$-Fe (para), $D_0 = 0.18 \text{ cm}^2 \text{ sec}^{-1}$, $Q = 64.5 \text{ k cal mole}^{-1}$ for $\gamma$-Fe). The volume diffusion mechanism gives theoretical migration velocities independent of bubble radius.

The vapour transport estimate is taken from equation (24) with $\beta_{vt} = 3/2$ using the expression for $D_v$ used by Speight (69). This gives the expression:

$$V = 0.1 \frac{p^r}{T^{3/2}} \text{ cms sec}^{-1}$$

where $p$ is the vapour pressure in dynes cm$^{-2}$ at $T^0 K$ and $r$ is the bubble radius in cms.

There appears to be considerable scatter in the published data for the vapour pressure of iron, but even an overestimate of 0.1 torr at $1550^\circ C$ gives a velocity of $0.2 \text{ sec}^{-1}$. Vapour transport is clearly not significant for these small bubble sizes.
It would not be appropriate to draw too many conclusions from so few results, but the following points can be made.

The migration velocity in the ferritic structure is at least as great as that predicted by the present theory for the surface diffusion mechanism. Even if there were some unforeseen error in the estimated temperature for TG5 and the temperature was as high as 910°C the rate would still only be a factor of two lower than the velocity estimated from Zahn's surface diffusion data. It is inconceivable that the migration rate at temperatures between 910°C and 1140°C (in the austenitic crystal structure) should have a faster migration rate than for the 1140°C result as both the surface diffusion and volume diffusion parameters drop in value considerably in the γ phase. The exception to this rule would be the vapour transport mechanism, but the vapour pressure of iron is too low for this mechanism to be significant.

The large difference in migration rate for the two ferritic results only 25°C different in temperature suggests an agreement with the high activation energy for surface diffusion found by Matsumura (71), Blakely and Mykura (72) and Zahn (73).

Unfortunately only one result was obtained for γ - Fe and this result is intermediate between the theoretical estimates using Blakely and Mykura's (72) surface diffusion data and those of Matsumura (71). The large values of $D_{\infty}$ and $Q_{s}$ found by Matsumura, Zahn and Blakely and Mykura indicates that unlike most b.c.c metals the surface diffusion mechanism is adatom diffusion (68).

The adatom can be regarded as the surface diffusion equivalent of the self-interstitial, and in a similar way (see equation (17)) the heat of transport for the atomic jump and the heat of formation of the adatom both contribute together towards the measured heat of transport. As the
A high value of $Q_s$ for the adatom is mainly due to the heat of formation of the adatom \(^{(88)}\), the migration energy being small, it is therefore reasonable to say.

\[ Q_s^* = q_a^* + h_a \Omega + q_a^* + Q_s \]  \hspace{1cm} (29)

As $q^*$, the heat of transport for the atomic jump, is going to be related in magnitude to heat of migration, although not necessarily equal to it \(^{(127)}\) \(^{(133)}\), and the heat of migration being small for the adatom, then it is reasonable to say.

\[ Q_s^* \Omega q_a^* + Q_s \Omega Q_s \]

This equality i.e. heat of transport = activation energy is often made with regard to thermal diffusion experiments simply because of the absence of any other criteria leading to a different estimate. In the case of surface diffusion by an adatom mechanism it is a more reasonable estimate simply because the activation energy for the diffusion process is dominated by the heat of formation and the rather more complex, and as yet unresolved, relationship between $q^*$ and $\Delta H_m$ is not so significant as it would be for a surface vacancy mechanism.

The theoretical curves in Figure (25) are drawn assuming $Q_s^* = Q_s$ and the reasonable agreement of the experimental results with these theoretical curves indicates that such an equality is reasonable. For the case of surface diffusion by a surface vacancy mechanism the situation would not be so simple. Reference to Table (I) shows how uncertain the magnitude (and at times the sign) of the heat of transport for volume diffusion is, and the same difficulties are found in analytically estimating the value
One interesting feature of the bubble migration distributions is the relatively narrow width of the band in the austenitic crystal structure compared with the two results in the ferritic structure. This would suggest that either the mechanism for bubble migration in γ-Fe results in a migration velocity which is independent of radius or that there was a rather more uniform bubble size in this particular specimen. It is interesting to note that Buescher and Meyer \(^{(85)}\) introduced the surface-gas mechanism concept to explain their results in uranium dioxide where they obtained radius independent migration with velocities \(10^6\) times too fast to be explained in terms of volume diffusion.

The mechanism proposed by Buescher and Meyer for the surface-gas mechanism gives a migration velocity \(V_{sg}\):

\[
V_{sg} = \frac{3 D_s \delta f Q_s}{kT r} v T
\]

where \(f\), the fraction of surface atoms excited into the surface-gas layer is given by:

\[
f = \frac{4 D_s}{N^2 a^2 v}
\]

where \(N\) is the number of interatomic distance \(a\) of the extended surface jumps proposed by this mechanism and \(v\) is the Debye frequency. Now assuming the equality \(Q_s = Q_s^*\), the ratio of the migration velocity by surface diffusion \(V_s\) to that by the surface-gas mechanism is:
\[
\frac{V_s}{V_{sg}} = \frac{N^2 a^2 v}{4 D_g}
\]

At 910°C, for \(\alpha\)-iron this evaluates to:

\[
\left[ \frac{V_s}{V_{sg}} \right]_{\alpha}^{910°C} = 0.13 N^2
\]

At 1140°C, for \(\gamma\)-iron:

\[
\left[ \frac{V_s}{V_{sg}} \right]_{\gamma}^{1140°C} = 0.11 N^2
\]

Therefore, in both cases, a surface jump of approximately three interatomic spacings would give a similar estimated bubble velocity for a 1000Å radius bubble. As \(D_g = T^{3/2}\),

\[
\frac{V_s}{V_{sg}} \propto T^{-3/2}
\]

therefore:

\[
\left[ \frac{V_s}{V_{sg}} \right]_{TG5}^{774°C} = 0.97
\]

\[
\left[ \frac{V_s}{V_{sg}} \right]_{TG6}^{751°C}
\]
Therefore the temperature dependence is not significantly different for the two mechanisms. Unfortunately in the absence of any radius dependence information it is not possible to say which of these two mechanisms is operative.

The only mechanism which has not been considered here is the interface controlled mechanism. In the absence of radius dependence data it is not possible to come to any satisfactory conclusion, but the fact that the migration rates are not slower than predicted by the surface diffusion mechanism suggests that interface control is not operative.

The line of bubbles in Figure (21a) is slightly curved. This is almost certainly because the higher temperature required for this austenitic migration experiment placed the bubbles closer to the heated surface of the specimen and therefore the temperature distribution is more sensitive to the power distribution on the electron bombarded surface. The maximum migration rate is in the centre of the specimen indicating that the power density was higher in the centre of the heated face as might be expected. The specimen could not be made longer because the evaporation rate becomes significant if a higher surface temperature is produced.
5.2 Discussion of Niobium Results

5.2.1 Average Bubble Size

The slope of the logr/logt plot (0.18 at 950°C to 0.19 at 1250°C) suggests very close agreement with the theoretical estimates of authors such as Gruber (69) (see equation (23)).

The computer based approach of Gruber and the complex analytical approach of Baroody (166) tends to obscure the importance of variables such as initial bubble size and these analyses also assume the perfect gas laws to be obeyed in order to simplify the calculations. Indeed, there is a danger that the simplifications needed to make the rigorous calculations possible may have themselves introduced larger errors than those resulting from a simpler analyses using the Van der Waal gas law. The main motive for these rigorous analyses was to eliminate the use of an 'average' bubble size so that the true distribution of bubble size can be incorporated into the calculations.

For this reason the error introduced by assuming an average bubble size has been investigated, and this is given in Appendix II. It can be seen from equation (II - 6) that starting from Chandrasekhar's (168) analysis as did Gruber but assuming an 'average' size for the bubbles results in a numerical coefficient of 1.35 compared with 1.30 in Gruber's size distribution analysis i.e. less than a 4% error. Baroody's analysis gives a constant of 1.33, less than a 2% error. Equation (II - 5) incorporating \( r_o \), the initial bubble size, gives an idea of the values of \( r_o \) for which the slope of the logr/logt plot is significantly influenced by the value of the initial bubble size. Clearly if \( r^5 >> r_o^5 \) then the initial bubble size can be neglected.

The simplification of assuming an average bubble size now makes
it possible to investigate the influence of non-ideal gas behaviour, which would be expected to be important for bubble sizes of the order of 100\AA.

For the case of helium in niobium the simpler form of the Van der Waals equation (see equation (II - 7)) is suitable. Assuming a value for \( \gamma \), the surface energy of niobium, of 2100 ergs cm\(^{-2}\) (207) and an atomic volume factor of 3.397 x 10\(^{-23}\) cm\(^3\) atom\(^{-1}\) (208), the number of helium atoms in a bubble of a given size can be calculated. This is plotted in Figure (36) for both the Van der Waal and ideal gas behaviour at 950\(^{\circ}\)C.

It can be seen that the number of helium atoms in the bubble is overestimated by the ideal gas equation by a factor of 2 for a radius of 90\AA and a factor of 3 at 40\AA. This would be expected to introduce significant errors into coalescence calculations.

The migration and coalescence equation for bubbles obeying the Van der Waal gas law is derived in Appendix II and is given by equation (II-3), which is of the form:

\[
f(r) - f(r_0) = 0.9 \left[ \frac{D_s a_o^4 m kT}{\gamma} \right]^t
\]

where \( m \) is the helium concentration

\( a_o \) is the lattice interatomic distance

\( D_s \) is the coefficient of surface self-diffusion

and \( f(r) \) is a complicated function of \( r \) and \( A \)

where \( A = \frac{2 \gamma b}{kT} \)

When \( A \) is small compared with \( r \), then the ideal gas law is a good approximation i.e. if \( A = 0 \) and \( r_0 = 0 \) is substituted into the above equation, then equation (II-6), which is similar to Gruber's result,
is obtained. For helium in niobium at 950°C \( A = 84.5 \) (\(^2\)). Therefore it is reasonable to put \( A = 0 \) for radii in excess of say, 1000\(^{\circ}\).

The most important difference between the equations is the value given to the

\[
\left[ \frac{D_s a_o^4 \text{mkT}}{\gamma} \right]
\]

term when the curve fitting is done for \( r < 1000 \). For example, if \( r = 37.5 \) at \( t = 1 \) hour at 950°C and \( r^5 \gg r_o^5 \), then assuming ideal gas law:-

\[
\left[ \frac{D_s a_o^4 \text{mkT}}{\gamma} \right] = 4.59 \times 10^{-37} \text{ c.g.s. units}
\]

Van der Waal law :-

\[
\left[ \frac{D_s a_o^4 \text{mkT}}{\gamma} \right] = 1.67 \times 10^{-37} \text{ c.g.s. units}
\]

Therefore \( D_s \) estimated from Gruber's equation would be a factor of 2.75 too high. Conversely if the values for \( D_s \), \( m \), \( T \) and \( \gamma \) are known then the calculated radius would be in error by 22%.

The effect of the Van der Waals coalescence equation on the slope of the \( \log r / \log t \) plot is small and the calculated slopes for the 950°C, 1050°C and 1250°C results shown in Figure (26) are 0.179, 0.182 and 0.188 respectively, which as can be seen from Table (4) is in excellent agreement with the regression lines through the experimental results.

There is no evidence of a decreased bubble size at the low duration end of the 950°C results (i.e. 0.25 hours) so it can be assumed that all the helium has precipitated out of solution into bubbles after a 950°C/1 hour
heat treatment, Speight (46) and Markworth (47) have analysed the rate of
growth of bubbles due to atomic inert gas diffusion from the matrix into
bubbles, but it is not considered that there is sufficient information from
the 850°C and 950°C results to make a meaningful estimate of the atomic
diffusion coefficient. It is also doubtful if these analyses are appropriate
as they assume that the bubbles are stationary and that growth occurs by
diffusion of inert gas atoms to the bubble. In the system investigated
here there is no evidence of immobile bubbles. Indeed the \( \frac{1}{5} \) slope of
the logr/logt plot suggests a surface diffusion mechanism with no restraint
imposed by dislocations (which would give a \( \frac{1}{7} \) slope (165)). Therefore
the bubbles formed during gas precipitation will be highly mobile and will
collect gas atoms as they move.

There appears to be a tendency towards decreased slope of the
logr/logt plot for radii in excess of 100\( \AA \), the 1050°C/100 hour and 1250°C/
6 hour results being rather lower than expected. (The calculated regression
lines ignored these two results). There are several possible explanations
for these results:

i) \textit{Channelling:}

It is possible that by chance these two results have a reduced
bubble size because in the foils available none had the helium concentration
that was intended. More results would be necessary to clarify this point.

ii) \textit{Diffusion of Bubbles out of the Original Helium Zone}

To assess the significance of this effect, drift distances due
to Brownian motion must be calculated as a function of bubble size. Some
values of \( D_B \) and the 100 hour drift distances (calculated from
\( d = \sqrt{\frac{6D_B t}{\pi}} \))
for bubbles of various sizes at 950°C, and 1250°C are given in Table (6).
It can be seen that a 1000\textdegree C radius bubble at 1250\textdegree C has a value for $D_B$ of $1.04 \times 10^{-15}$ cm$^2$/sec$^{-1}$. We now consider the behaviour of this bubble as it migrates through the lattice. The 1000\textdegree C bubble would be formed after about 0.4 hours at 1250\textdegree C. After a 2 hour lifetime on average it will have coalesced with another 'average' bubble to form a bubble with a radius of approximately 1400\textdegree (i.e. $\sqrt{2}r$, assuming ideal gas laws for simplicity). In this 2 hours it will have drifted on average 670\textdegree. Repeating this argument for the next coalescence, a 2000\textdegree bubble will be formed after another 14 hours, the average drift of the 1400\textdegree bubble being about 837\textdegree. So we see that we have now formed a 2000\textdegree radius bubble from a region at 0.4 hours well within the linear part of the log$r$/log$t$ plot and have arrived at a bubble radius well in excess of the reduced radius results in question and have drifted a total distance of 1557\textdegree. In fact the results being considered are virtually within the range of the first coalescence event considered here. It is therefore concluded that bubble drift from the helium band is not significant and would only produce minor errors.

The 1050\textdegree C/100 hour average radius result is low, but there is a straight line relationship through the 1250\textdegree C results that suggests that bubble growth can proceed to sizes beyond that of the 1050\textdegree C/100 hours result (1070\textdegree radius) without a reduction in slope due to bubble drift from the implanted region.

iii) Influence of Dislocations

Speight (165) has analysed the random migration and coalescence mechanism of bubble growth for the situation where all the bubbles are on dislocations and are only free to move along the dislocations. For this situation he arrives at a relationship $r = t^{1/7}$ which would therefore lead to a slope on a log$r$/log$t$ plot of 1/7 (instead of 1/5). This is a
possible explanation for the low results, Weeks et al (107) have analysed the interaction of a bubble with a dislocation and concluded that there is a significant attractive force. Martin (117) has come to a different conclusion, but his analysis was for an equilibrium bubble where the vacancy supply was sufficient to maintain the equilibrium size of the bubble as it interacts with the stress field. Under these conditions the interaction can be repulsive as the gas volume and surface area effects then dominate the attractive stress field interaction. Weeks et al (107) only considered the elastic interaction. The exact nature of the stress field in the neighbourhood of a dislocation and the precise interaction of the bubble is a complex problem and it is difficult to decide from the theoretical analyses which interaction to expect. It is very likely, of course, that bubbles nucleated on dislocations will stay on dislocations due to the strain energy of the dislocation in the material removed by the presence of the bubble. The effect of dislocations can only be evaluated by studying material with high dislocations densities so that in the sort of drift distances considered in the previous section there is a significant probability of interaction with a dislocation.

It is concluded that if the dislocation/bubble interaction is attractive then a decreasing slope would be expected due to an increasing fraction of bubbles being captured by dislocations. Martin (117) has suggested that for equilibrium bubbles the interaction would be repulsive in which case the above argument would not apply. No attempt was made to specifically set out to measure dislocation densities or to ascertain the fraction of bubbles on dislocations. Nevertheless, the photographs taken of the two specimens (1050°C/100 hours and 1250°C/6 hours) which showed a lower average bubble radius than expected showed no evidence of increased dislocation density or increased dislocation/bubble interaction. As the
dislocation structure had been stabilised by the pre-implant 1350°C anneal, then the dislocation structure would be expected to be similar for all post-irradiation anneals carried out at lower temperatures. Therefore if the low bubble radius result at 1050°C/100 hours were due to dislocations, then a similar effect would be expected for most of the 1250°C results (which have larger average radii) and this was not found.

In the absence of experimental information to the contrary it is concluded that the first explanation i.e. the channelling effect, is the most likely explanation. To achieve this reduction in bubble radius (80% of that expected in the worst case (1050°C/100 hours) ) merely by a reduced bubble concentration would require a fractional concentration reduction to (0.8)^5 i.e. about 1/3 of the intended concentration. This means that if the concentration of bubbles and therefore the helium atom density is to be estimated from the bubble density in the foil, then the foil thickness must be measured to significantly better than a factor of three.

Stereomicroscopy was attempted, but the lack of suitable surface markers made this difficult. The density of \(10^{-7}\) radius bubbles which would account for the implanted concentration is \(7.8 \times 10^{10}\) bubbles \(\text{cm}^{-2}\) per 1000\(\AA\) foil thickness. The measured density was \(3.8 \times 10^{10}\) bubbles \(\text{cm}^{-2}\). If the foil were 1500\(\AA\) thick, then the ratio is about 3:1 as predicted. The 1050\(°\)C/25 hour micrograph had \(1.7 \times 10^{11}\) bubbles \(\text{cm}^{-2}\) of average radius 94\(\AA\) and assuming a 1500\(\AA\) foil thickness this accounts for the implanted concentration. Therefore it would appear that a low helium concentration is probably responsible for the low bubble radius for the 1050°C/100 hour anneal.

5.2.2 Surface Diffusion Constant from Average Bubble Size Results

Calculating the activation energy for surface diffusion by plotting
log $rT^{1/5}$ against $1/T$ as mentioned previously gives an approximate value due to the deviation from ideal gas behaviour. Calculating from the intercepts of the least squares regression line through the results at various durations gives a range of results for the activation energy from 68 to 80 k cal mole$^{-1}$.

The most accurate assessment would come from fitting the non-ideal gas equation to the results at each temperature. Figure (37) shows the values of $D_0$ calculated in this way. One set of results at 950°C, 1050°C and 1250°C is obtained from the best fit to the average results and the other is a line through the largest average radius result found at each temperature when results were available from more than one specimen. This latter technique is appropriate because the most significant error is likely to be low results due to channelling rather than random errors. The line drawn through the high value results and the single 1450°C result gives $Q_s = 82$ k cal mole$^{-1}$ and

$$D_0 = 3.0 \times 10^3 \text{ cm}^2 \text{ sec}^{-1}.$$ 

It would appear that niobium is similar to iron in having unusually high values for these constants for a b.c.c. metal suggesting that both metals may have an adatom surface diffusion mechanism.

5.2.3 Bubble Size Distribution

When the presence of 'peaks' in the size distributions was first noticed, it was assumed that this was almost certainly due to there being a fairly precise initial bubble size. It was soon realised that this effect was quite pronounced in specimens where this could not be the explanation. For example, specimen H25G, given a heat treatment of 1050°C for one hour shows a well defined structure. The three peaks in H25G have gas
atom ratios of $1:2:3$ with approximate helium contents of 7550 atoms, 7550 x 2 and 7550 x 3 atoms for the three peaks. The peak positions at 23$\AA$ and 38$\AA$ radius in specimen H71A, annealed at 1050$^\circ$C/4 hour have gas contents of 1160 and 4552 atoms, the ratio being 1:4. The peaks in H71A are admittedly not particularly well defined, due possibly to the small number of bubbles counted, but it illustrates the general principle that even though peaks invariably have simple integral ratio of gas atoms for the peak bubbles sizes, the peaks in two distributions at the same temperature but different durations invariably do not have any simple relationship with each other. This would suggest that there are not specific preferred sizes which make up the distribution with the annealing duration determining the relative abundances of these sizes. This might be the effect expected if the initial bubble distribution at a particular temperature was dominating the distribution pattern. The evidence appears to suggest that the dominant factor is the ratios within a distribution rather than the values themselves.

Because of the interest in the initial bubble distribution which would require looking at results at small bubbles sizes, the 950$^\circ$C range of specimens was measured with particular accuracy. The results are displayed in Figure (29).

The low duration anneals at 950$^\circ$C are difficult to interpret because there are so many peaks and the numbers of bubbles represented by each peak is quite small and therefore leads to a low statistical confidence. But there is little doubt that 'peaks' really do exist. For example when two prints have been taken from two areas of one plate, the distributions in each print are similar, although sometimes slightly displaced. This displacement is noticeable in many of the results and perhaps erroneously leads to a conclusion when the results from many prints are added together.
that the structure does not exist but is a 'statistical' effect. The presence of this displacement is a common effect (see Figure 50 (c)) and is shown by long duration tests as well. This displacement is possibly due to magnification errors.

Long duration results such as H59C show the 'peak' structure in a convincing manner. Each peak now has several results building up the shape of each peak rather than the alternate high and low results found at low durations which are not particularly convincing. The ratios of the major peaks in H59C are in the ratio 1:2:3:4:5, these being multiples of 13,250 He atoms or approximately 20 19Å radius bubbles. It is evident that the random migration and coalescence assumptions used in the distribution analysis of Gruber resulting in a simple skew distribution does not apply in this case.

The rather more complex structure of the distribution for short duration anneals at 950°C is possibly due to the presence of a fairly discrete initial bubble size, possibly about 16Å radius (approximately 400 He atoms), as the lowest peaks for the 950°C/1 hour and 950°C/2 hour results seem to be multiples of approximately 400 atoms.

We must now investigate what deviations from the idealised random migration and coalescence upon contact model could account for the production of this type of distribution.

Let us consider deviations from randomness in the migration. This implies that specific directed forces are influencing the migration of the bubble.

i) Stress Fields of other Non-equilibrium Bubbles

There is a possibility that if vacancies are not sufficiently readily available, particularly at low temperatures, that a recently
coalesced bubble might have a significant lifetime with an excess pressure thus producing a strain field with which other bubbles could interact.

If two bubbles, radius \( r_1 \), with equilibrium internal pressures

\[
\frac{2\gamma}{r_1}
\]

coalesce, they will form as a first stage of coalescence a bubble of radius \( r_2 = \frac{3}{2} r_1 \), i.e., a constant volume process. But the equilibrium size \( r_3 \) has a radius \( r_3 = \frac{2}{5} r_1 \) (assuming the ideal gas laws for simplicity) and an equilibrium pressure

\[
\frac{2\gamma}{r_3} = \frac{2\gamma}{\sqrt{\frac{2}{2}} r_1} = \frac{\sqrt{2}\gamma}{r_1}.
\]

Therefore immediately after coalescence the bubble has an excess pressure

\[
P_e = \frac{2\gamma}{r_1} - \frac{\sqrt{2}\gamma}{r_1} = \frac{0.59\gamma}{r_1}
\]

Greenwood et al \((40)\) have derived an equation for the rate of growth of a bubble with an excess pressure as controlled by the rate of supply of vacancies:

\[
\frac{dr}{dt} = \frac{D_v c_e v (p - \frac{2\gamma}{r})}{r k T}
\]

where \( D_v \) is the vacancy diffusion coefficient

\( c_e v \) is the equilibrium concentration of vacancies at temperature \( T \)

and \( (p - \frac{2\gamma}{r}) \) is the excess pressure.

If we now substitute the excess pressure produced by two equal bubbles into this equation and express in terms of volume instead of radius we get:
where \( \frac{dv}{dt} \) is the initial rate of volume increase.

Substituting values into this expression for niobium at 950°C gives an initial rate of volume increase of approximately \( 10^{-9} \) atomic volumes per second independent of bubble radius. As a 100Å radius bubble contains approximately \( 10^5 \) atomic volumes, it is clear that the rate of approach to the equilibrium pressure is going to be slow. This is in disagreement with the fact that all the bubbles seen in the niobium foils were faceted and bubbles with an excess pressure would be expected to be spherical.

Comparing this with the duration between coalescence events (a 50Å bubble takes on average approximately 100 hours at 950°C to coalesce with a similar sized bubble to form a bubble of approximately 70Å radius) it is evident that the non-equilibrium period of time after coalescence is longer than the coalescence time and might cause a significant departure from random migration and coalescence conditions.

It is therefore concluded that a departure from random migration and coalescence conditions due to the presence of a significant fraction of non-equilibrium bubbles should be found.

ii) Stress Fields of Equilibrium Bubbles

It has been pointed out by Lidiard and Nelson (59) that equilibrium bubbles can have a stress field associated with them equivalent to an excess pressure of

\[
\frac{2(\sigma - \gamma)}{r}
\]
where $\sigma$ is the surface energy
and $\gamma$ is the surface tension.

There is therefore the possibility of bubble interaction in a system composed only of equilibrium bubbles.

The interaction of a bubble with a stress gradient has been analysed by Eyre and Bullough \((216)\), Lieden and Nichols \((58)\) and Martin \((117)\). The interaction between two bubbles has been analysed by Willis and Bullough \((57)\) and Lieden and Nichols \((58)\). The analyses by Eyre and Bullough \((210)\) and Lieden and Nichols for a constant volume bubble in a stress gradient showed that the bubble migrates to a region of higher stress for both compressive and tensile stress gradients. The analysis of Martin \((117)\) for an equilibrium gas bubble showed that the bubble migrates to a region of lower stress. The two analyses for the bubble interaction problem considered the constant volume situation and as would be expected showed there to be an attraction between two bubbles provided at least one of them had a non-equilibrium gas pressure. Applying Martin's analysis to the interaction of two equilibrium bubbles would lead to the conclusion that the interaction would oppose coalescence. The difference between the two types of analysis is caused by the effect of the gas volume change and surface area change as the bubble changes size when it moves along the stress gradient.

Combining the two types of interaction, i.e. the elastic interaction and the size change effect, to the case of the interaction between two bubbles is difficult. As the elastic interaction energy is proportional to $\ell^{-6}$ \((56)\) \((57)\) \((58)\) where $\ell$ is the separation of the surfaces of the two bubbles, it would make the calculation of the size change very difficult as the interaction would change considerably over distances small compared with the radius of the bubble.
The elastic interaction equation derived by Eshelby (56) is of the form:

\[ E_{\text{int}} = -\frac{A}{6\epsilon} r_1^3 r_2^3 \left( p_1^2 r_1^3 + p_2^2 r_2^3 \right) \]  

(31)

where \( r_1, r_2 \) are the radii of the bubbles, \( \epsilon \) is the surface separation, and \( p_1, p_2 \) are the excess pressures in the bubbles. \( A \) is a constant.

If we substitute

\[ p_1 = \frac{2 (\sigma - \gamma)}{r_1}, \quad p_2 = \frac{2 (\sigma - \gamma)}{r_2} \]

and

\[ F_{\text{int}} = -\left( \frac{dE_{\text{int}}}{d\epsilon} \right) \]

we get:

\[ F = r_1^3 r_2^3 (r_1 + r_2) \]

For a surface diffusion mechanism the bubble mobility is proportional to \( \frac{1}{r^4} \).

Therefore the velocity of approach for the two bubbles is:

\[ V = \frac{B r_1^3 r_2^3 (r_1 + r_2)}{r_1^4} + \frac{B r_1^3 r_2^3 (r_1 + r_2)}{r_2^4} \]

where the first term is the migration velocity of the bubble radius \( r_1 \) and the second term the velocity of the bubble radius \( r_2 \), and
B is a constant.

If both bubbles have radius $r$ then:

$$V_{(r,r)} = 2Br^3$$

If one bubble is radius $r$, the other $2r$

$$V_{(r,2r)} = 24 Br^3 + \frac{3}{2} Br^3 = \frac{51}{2} Br^3$$

If both bubbles of radius $2r$,

$$V_{(2r,2r)} = 32Br^3$$

This shows that the approach velocity due to elastic interaction is much higher for two large bubbles or a large and a small bubble than it is for two small bubbles.

Therefore small bubbles are more likely to coalesce with larger bubbles than coalesce with each other. This would tend to decrease the population of radii on the small radius end of the distribution (compared with the skew distribution predicted by Gruber (68)). This simple argument is based on the attractive elastic interaction contribution only; the effect of the size change contribution to the interaction, which is more difficult to quantify, has not been considered.

This type of size selective interaction is the most likely explanation for the evidence of size distributions developing that would not be expected for random migration and coalescence. Lidiard and Nelson (59) have suggested that when $\lambda < 3r$ this type of interaction could impose a significant drift upon the random motion of the bubbles. For the helium concentration implanted in this experimental programme, the average distance between 100\(\AA\) radius bubbles is about 500\(\AA\) and therefore close to the distances
where elastic interactions can become significant.

iii) Dislocation Interaction

Dislocation interaction is another possible cause of non-random migration behaviour, but the average bubble size results suggest that it is not significant. Even if it were significant, no mechanism is evident that would cause the distributions found.

It is concluded that the bubble size distributions found are evidence of a deviation from the simple random migration and coalescence model, and it is suggested that this is caused by the interaction of the stress fields of equilibrium bubbles.
6. CONCLUSIONS

6.1 Temperature Gradient in Iron

i) helium bubbles in a temperature gradient of about 1000°C move up the temperature gradient.

ii) the rate of migration is consistent with theories of migration by a surface diffusion mechanism or possibly a surface-gas mechanism. The volume diffusion and vapour transport mechanism theoretical predictions give migration rates at least an order of magnitude too slow. As the migration rate was not slower than predicted by the surface diffusion mechanism it is concluded that an interface controlled mechanism is not operative.

iii) the relative migration velocities in α and γ-Fe are consistent with published surface diffusion data for these two structure.

iv) the measured heat of transport for surface diffusion $Q_s^*$ is positive. It is suggested that the surface transport entity is the adatom and that as a consequence of the high formation energy and low migration energy for this entity that the approximate equality $Q_s^* \approx \frac{1}{2} S$ is reasonable. The scatter in the available surface diffusion data does not make it possible to experimentally justify this equality, but the few results obtained are not inconsistent with it.

6.2 Migration and Coalescence in Niobium

i) the migration mechanism for helium bubbles in niobium is surface diffusion.

ii) the high values obtained for $\lambda_s$ and $D_0$ suggest that
like iron the surface diffusion entity is the adatom.

iii) the slope of the logr/logt plot indicates that the dislocation density was not high enough in the fully annealed niobium to significantly influence the migration of the helium bubbles.

iv) the bubbles are faceted, but there is no evidence that the faceting is causing a significant interface controlled limitation to the bubble mobility.

v) the distribution of bubble sizes found suggests that the migration and coalescence is not a random process as the simple skew distribution that would be expected is not found. Interaction of the stress fields of the bubbles is suggested to be the cause of non-random behaviour.

vi) it has been shown that approximating to an average radius in the theoretical treatment of migration and coalescence does not lead to serious errors. Far more serious errors can be introduced for small bubble sizes by approximating to ideal gas behaviour in the bubbles. An expression has been derived for random migration and coalescence using the Van der Waal gas law.
Appendix I

A Technique for the Preparation of Thin Foils from Metal Surfaces

There are many investigations in metallurgy which require a transmission electron microscopy investigation 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 (210) in a P.T.F.E. holder (198) with the surface protected with a masking lacquer. 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.

It was required to produce foils from niobium which had been irradiated with helium ions and then annealed to produce bubbles. Approximately 3000Å was removed by anodic stripping and foils were then required to measure bubble sizes in the next 1000-1500Å of material. The electrolyte used for electro-thinning Nb is 10% HF / H₂SO₄ and no lacquer could be found that would protect the ion implanted region around the foil perforation. The P.T.F.E. holder technique combined with a light source and photocell could be used to switch off the electropolishing current as soon as a very small perforation formed, so that the time available for the electrolyte to penetrate between the foil and the lacquer is minimised. Even with these precautions, the success rate was too low to be of any practical use.

Consequently, a new technique has been developed that is not only capable of producing 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 observation of the progress of electropolishing being necessary, and no expensive and cumbersome electro-optical system is needed.

The method is illustrated in Figure 38. The surface to be protected is in contact with an organic liquid which is at a positive pressure with respect to electrolyte, the magnitude of this pressure being controlled by the 'head' of liquid. The liquid must satisfy the following conditions:

a) it must be immiscible with the electrolyte
b) it must not react significantly with the electrolyte
c) it must be an electrical non-conductor
d) it must have a higher density than the electrolyte
e) it must not react with the specimen

If the above conditions are satisfied, the liquid will flow through the perforation in the foil, with cover the specimen and isolate the specimen both chemically and electrically from the electrolyte (particularly useful for electrolytes which 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 is best used at a temperature of 60°C and the electrolyte must be stirred if a good polish is to be obtained in a reasonable time. The electrolyte, being 90\% \text{H}_2\text{SO}_4, has 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 39. The holder is made of P.T.F.E. and is approximately 1 3/4" in diameter and 2 1/2" high, the internal diameter being about 1 1/2" diameter. The geometry in the region of the specimen (see Figure 38) is quite critical for niobium. If the edge thickness is much more than 0.010", stable bubbles will form as the flow of electrolyte produced by 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 to 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, 3 mm o.d. and 2 mm i.d. (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, being careful that an air lock is not formed (wetting the tube with methanol helps to prevent bubbles
being trapped in the tube). If the liquid leaks out, the spring tension can be increased, as the disc may not be flat (the niobium used here was only 0.002" 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. The electropolishing conditions are given in Table 7. The method is somewhat simpler for iron as neither stirring or heating are required.

For niobium, 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 r.p.m. close to the surface of the specimen has been found most suitable.
Appendix II

Migration and Coalescence Equations

The most rigorous analysis has been that due to Gruber (68). This theory is based on the analogous problem of colloid coagulation as treated by Chandrasekhar (168) who derived:

\[ J_{i+k} = 4 \pi D_{ik} \cdot R_{ik} \cdot v_i \cdot v_k \left( 1 + \frac{R_{ij}}{(\pi D_{ij} t)^{1/2}} \right) \]  (26)

In the case of bubble coalescence \( J_{i+k} \) is the coalescence rate between bubbles of radius \( r_i, r_j \); \( v_i \) and \( v_k \) are the respective concentrations of these bubbles and \( R_{ij} \) is the interaction distance \( (r_i + r_k) \). The diffusion coefficient \( D_{ik} \) is shown by Chandrasekhar to be given by \( (D_i + D_k) \). If the mean distance travelled by the two bubbles relative to one another is large compared with the sum of the bubble radii, then the term in brackets at the end of equation (26) can be neglected.

\[ J_{i+k} = 4 \pi (D_i + D_k) (r_i + r_k) \cdot v_i \cdot v_k \]  (27)

Using this equation, Gruber (68) has produced a computer based analysis. These calculations together with a subsequent curve fitting technique gave an equation for the average radius:

\[ r = 1.30 \left( \frac{m k T a_o^4 D_s t}{\gamma} \right)^{1/5} \]  (28)
where \( m \) is the gas concentration
\( a_0 \) is the interatomic distance
\( D_s \) is the coefficient of surface self diffusion

The initial bubble size is assumed to be the monatomic gas atom. Baroody's (166) analysis gives a constant of 1.33.

It is therefore possible to investigate the inaccuracies introduced by assuming an average bubble size, ignoring the size distribution, as is necessary with an analysis not using a computer, by comparing the result with the above equation.

If, in equation (27)
\[
D_i = D_k = D
\]
\[
r_i = r_k = r \quad \text{(the average bubble size)}
\]
\[
v_i = v_k = c
\]
Then \( J = 16 \pi D r c^2 \) \hspace{1cm} (II-1)

For each coalescence event, the number of bubbles is reduced by one:

Therefore \( J = \frac{dc}{dt} \)

Assuming the perfect gas laws,
\[ pV = n k T \]

If the bubble is at equilibrium pressure
\[ p = \frac{2\gamma}{r} \]

Substituting
\[ V = \frac{4}{3} \pi r^3 ; \quad nc = m \]
Therefore \( r^2_c = \frac{3 m \kappa T}{8 \pi \gamma} \) \( \text{(II-2)} \)

Therefore \( J = \frac{-dc}{dt} = \frac{2}{r^3} \cdot \frac{dr}{dt} \left[ \frac{-3 m \kappa T}{8 \pi \gamma} \right] \) \( \text{(II-3)} \)

Substituting equation (II-2) into equation (II-1)

\[
J = 16 \pi D r \left[ \frac{3 m \kappa T}{8 \pi \gamma} \right]^{2} \cdot \frac{1}{r^4}
\]

Substituting

\[ D = 0.3 D_s \left( \frac{a^4}{r} \right) \] (see reference 68)

Therefore \( J = \frac{4.8 \pi D_s a_0^4}{r^7} \left[ \frac{3 m \kappa T}{8 \pi \gamma} \right]^2 \) \( \text{(II-4)} \)

Equating the two expressions for \( J \) (equations (II-3) and (II-4)), and integrating:

\[
r^5 - r_0^5 = 9 \frac{D_s a_0^4 m \kappa T}{2 \gamma} t \] \( \text{(II-5)} \)

To compare with the calculated result of Gruber, put \( r_0 \) (the initial bubble size) equal to zero i.e. \( r^5 \gg r_o^5 \)

\[
r = 1.35 \left[ \frac{D_s a_0^4 m \kappa T}{\gamma} t \right]^{1/5} \] \( \text{(II-6)} \)

This compares with a numerical coefficient of 1.30 in Gruber's computer calculations and 1.33 in Baroody's calculations. It is concluded
that approximating the bubble size to an average value does not introduce serious errors.

One of the assumptions made in the above calculations and in all the published theories is the application of the ideal gas laws. The above calculations are amenable to the application of Van der Waals equation:

\[ p (V - nb) = n k T \]  

(II-7)

at the expense of mathematical complexity.

This form of Van der Waals equation is considered to be appropriate for helium bubbles (4), but not for the heavier inert gases.

The resulting equation is:

\[ f(r) - f(r_0) = 0.9 \left[ \frac{D S a^4}{Y} \right] t \]  

(II-8)

where

\[
f(r) = \left\{ \frac{8r^6 + 3Ar^5 - 5A^2 r^4 + 10A^3 r^3 - 30A^4 r^2 - 60A^5 r}{40 (r + A)} \right\} + 1.5 A^5 \log_e (r + A)
\]

and \( A = \frac{2 \gamma b}{kT} = 84.54 \text{ (Å) for He in Nb at 950°C} \)

and \( \gamma = 2100 \text{ ergs cm}^{-2} \).

\( b = 3.397 \times 10^{-23} \text{ cm}^3 \text{ atom}^{-1}; \) for niobium.
Other Diffusion Mechanisms

For volume diffusion and vapour transport mechanisms:

\[ D_B \propto r^{-3} \]

Therefore equation (II-4) becomes:

\[ J \propto r^{-6} \]

Equating this with equation (II-3) gives

\[ r \propto t^4 \]

for \[ r^4 \gg r_0^4 \]

i.e. logr/logt plot will have a slope of \( \frac{1}{4} \).
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142) P. Therungvist & A. Lodding,

143) A. Lodding & P. Therungvist,

144) J.H. Matlock & J.P. Stark,

145) L.C.C. da Silva & R.F. Mehl,

146) W.G. Brammar,

147) C.J. Meechan & C.W. Lehmann,

148) H.B. Huntington & A.R. Grone,

149) R.V. Penney,

150) D. Jaffe & F.G. Shewmon,

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178) R.E. Carter, J.H. Rosolowski & J.J. Madeau,

179) T.R. Anthony & H.E. Cline,


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196) L. Young,
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Fig 1. The Terrace - Ledge - Kink Model of a surface.

Fig 2. Variation of Surface Diffusion Coefficient with Temperature and Mechanism.
Fig 3. Surface Diffusion Coefficient for Various B.C.C. metals as a function of Temperature.

Fig 4. Mass Transport by Vacancies in a Pure Metal.
   a) before thermal diffusion
   b) after thermal diffusion
Fig 6. Photograph of Accelerator.
Fig. 7. Accelerator Ion Source.
Fig. 8. Accelerator Tube.

- Extraction electrode.
- Centre electrode.
- Movable focussing electrode.

3" long, 4" i.d. glass pipe section.
Fig. 9a. Target Chamber (side view).

- **Target**
- **Window**
- **Electrical leadthroughs**
- **Ionization gauge**
- **Liquid nitrogen cold finger**
- **2" diffusion pump with liquid nitrogen trap**
- **Baffle**
- **Beam**
Fig. 9b. Target Chamber (end view).

- Pumped interspace between shaft's or ring seals.
- Cooling tubes.
- Copper cooling block.
- Vacuum lock.
Fig. 10. Target Region Geometry.
ionisation gauge.

heat shields.

isothermal annealing crucible.

glass vessel.

electron bombarding filament (temperature gradient)

electron bombarding filament

water cooled copper block.

2" diffusion pump.

Fig. 11. Annealing Furnace.
Fig. 12. Electron Bombardment Geometry for Temperature Gradient Anneals.
Fig. 13. Sputter Cleaning and Iron Deposition Apparatus.
Fig 15. Scanning electron micrograph of iron surface after 50keV helium ion implantation to a dose of $7.5 \times 10^{17}$ ions cm$^{-2}$ at room temperature.
Fig 16. Scanning electron micrograph of iron surface after 50keV helium ion implantation to a dose of $10^{16}$ ions cm$^{-2}$ at room temperature and $2 \times 10^{16}$ ions cm$^{-2}$ at 600°C.
Fig 17. Scanning electron micrograph of iron surface after 50keV helium ion implantation to a dose of $10^{16}$ ions cm$^{-2}$ at room temperature and $4 \times 10^{16}$ ions cm$^{-2}$ at 850°C.
Fig. 18. Electropolishing through a bubble.
Fig 19. Grain size discontinuity in a calibration specimen.
Fig. 20. Thermal Conductivity of Iron.
Fig. 21. Temperature and Temperature Gradient in the Iron Specimens.
Fig 22. Migration of bubbles up temperature gradient in Specimen T05 (α-iron).
Fig 23. Migration of bubbles up temperature gradient in Specimen TG6 (\(\alpha\)-iron).
Fig 24. Migration of bubbles up temperature gradient in Specimen TG8 (γ-iron).
Fig. 25. Experimental and Calculated migration rates for 1000 Å radius bubbles in 1000°C cm⁻¹ temperature gradient.
Fig. 26. Migration and Coalescence Results for helium bubbles in Niobium.
Fig. 27. Temperature Dependence of Bubble Radius after 1 hour heat treatment.
Fig 28. Typical helium bubble micrographs.
Specimen H74A
950°C/¼ hr.
32 bubbles measured.
Measuring Interval 1.0Å

Specimen H73B
950°C/½ hr.
51 bubbles measured.
Measuring Interval 1.0Å

Fig. 29a Bubble size distributions for Niobium
Specimens heat treated at 950°C.
Specimen H67A
950°C / 25 hrs.
50 bubbles measured.
Measuring Interval 5.7Å

Specimen H59C
950°C / 100 hrs.
69 bubbles measured.
Measuring Interval 1.6Å

↑ ↑ ↑ ↑ ↑ ↑ ↑
Gas atom ratio 1 : 2 : 3 : 4 : 5 : 6
radius (Å) →

Fig. 29b. Bubble size distributions for Niobium Specimens heat treated at 950°C.
Fig. 30a Bubble size distributions for Niobium Specimens heat treated at 1050°C.
Specimen H77A
1050°C/25hrs.
97 bubbles measured.
Measuring Interval
4.1 Å

Specimen H78B
1050°C/100hrs.
89 bubbles measured.
Measuring Interval
4.1 Å

Fig. 30b. Bubble size distributions for Niobium.
Specimens heat treated at 1050°C.
Specimen H21A
1250°C/½ hr.
47 bubbles measured.
Measuring Interval 5.7 Å

Specimen H27D
1250°C/6 hrs.
64 bubbles measured.
Measuring Interval 12.2 Å

Fig. 31. Bubble size distributions for Niobium.
Specimens heat treated at 1250°C.
Fig 32. Bubble size distributions in two different areas of the same plate.
Fig 33.
Optical micrograph of 100keV helium implanted specimen with 1150°C/1 hr heat treatment and 4400Å removed by anodising.

Fig 34.
Optical micrograph of 100keV helium implanted specimen with 1150°C/1 hr heat treatment and 7500Å removed by anodising.
Fig 35. Micrograph of specimen H21 showing 'rings' round some bubbles.
Fig. 36. Number of helium atoms in bubble at 950°C.
Fig. 37. Surface Diffusion Coefficient of Niobium as a function of Temperature.
Fig. 38. Thin Foil Preparation Technique.
head of liquid controls pressure differential across specimen.

Platinum wire cathode

Electrolyte

Specimen

PTFE container

Organic liquid

Heater block

Anode

Tube spring loaded against specimen

Polythene tube

Fig. 39. Thin Foil Preparation Apparatus.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Reference</th>
<th>$Q_1^*$ kcal/mole</th>
<th>$Q_1^<em>(q_1^</em>)$ kcal/mole</th>
<th>$Q$ kcal/mole</th>
<th>$\Delta h_m$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>(138)</td>
<td>0</td>
<td>9.0</td>
<td>23.0</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>(139)</td>
<td>-2.3</td>
<td>6.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(151)</td>
<td>+3.9</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>(147)</td>
<td>3.0</td>
<td>29.9</td>
<td>48.0</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>(150)</td>
<td>-7.2</td>
<td>19.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(154)</td>
<td>0</td>
<td>26.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Fe</td>
<td>(146)</td>
<td>0</td>
<td>+9.2</td>
<td>57.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(154)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Fe</td>
<td>(155)</td>
<td>0</td>
<td></td>
<td>64.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(156)</td>
<td>25-100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>(141)</td>
<td>167-633</td>
<td></td>
<td>65.0</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>(157)</td>
<td>&lt;0</td>
<td>&lt;32.8</td>
<td>69.8</td>
<td>34.6</td>
</tr>
<tr>
<td>Ag</td>
<td>(154)</td>
<td>0</td>
<td>23.8</td>
<td>44.1</td>
<td>19.1</td>
</tr>
<tr>
<td>Au</td>
<td>(147)</td>
<td>-4.8</td>
<td>17.8</td>
<td>41.7</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>(150)</td>
<td>-8.6</td>
<td>14.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(154)</td>
<td>0</td>
<td>22.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>(140)</td>
<td>15.7</td>
<td>46.4</td>
<td>68.2</td>
<td>34.1</td>
</tr>
<tr>
<td>Al</td>
<td>(158)</td>
<td>-1.5</td>
<td>17.5</td>
<td>34.0</td>
<td>14.3-16.5</td>
</tr>
<tr>
<td></td>
<td>(144)</td>
<td>+11 (single xl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(144)</td>
<td>-2 (poly xl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-2r</td>
<td>(159)</td>
<td>-115</td>
<td>*</td>
<td>19.6†</td>
<td></td>
</tr>
<tr>
<td>β-Ti</td>
<td>(159) (141)</td>
<td>185</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>(143)</td>
<td>12.2</td>
<td>21.7*</td>
<td>13.2</td>
<td>4</td>
</tr>
<tr>
<td>Pb</td>
<td>(142)</td>
<td>2.1</td>
<td>&gt;14.3</td>
<td>25</td>
<td>&lt;12</td>
</tr>
</tbody>
</table>
### Table 2

**Temperature gradient results**

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Electron Bombardment Power (watts)</th>
<th>Calculated temperature at bubbles from power input (°C)</th>
<th>Calculated temperature at bubbles from grain size discontinuity (°C)</th>
<th>Temperature gradient (°C cm⁻¹)</th>
<th>Migration distance (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG5</td>
<td>24.7</td>
<td>774</td>
<td>-</td>
<td>1278</td>
<td>100*</td>
</tr>
<tr>
<td>TG6</td>
<td>24.0</td>
<td>751</td>
<td>-</td>
<td>1242</td>
<td>20*</td>
</tr>
<tr>
<td>TG8</td>
<td>27.8</td>
<td>1141</td>
<td>1137</td>
<td>1437</td>
<td>157</td>
</tr>
</tbody>
</table>

* maximum rates i.e. leading edge of migrated bubble band.
### Micro-hardness results

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Heat Treatments</th>
<th>Comments</th>
<th>Hardness (Vickers)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre-irr</td>
<td>Post irr.</td>
<td>(Vickers)</td>
</tr>
<tr>
<td>Nb</td>
<td>-</td>
<td>-</td>
<td>As received</td>
</tr>
<tr>
<td>H1</td>
<td>1250/1hr</td>
<td>-</td>
<td>Recrystallised</td>
</tr>
<tr>
<td>H2</td>
<td>1250/1hr</td>
<td>-</td>
<td>Not recrystallised</td>
</tr>
<tr>
<td>H5</td>
<td>1250/1hr</td>
<td>1250/1hr</td>
<td>-</td>
</tr>
<tr>
<td>H20</td>
<td>1350/1hr</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H26</td>
<td>1350/1hr</td>
<td>1250/24hrs</td>
<td>*</td>
</tr>
<tr>
<td>H27</td>
<td>1350/1hr</td>
<td>1250/6hrs</td>
<td>-</td>
</tr>
<tr>
<td>H28</td>
<td>1350/1hr</td>
<td>1350/1hr</td>
<td>-</td>
</tr>
</tbody>
</table>

* Poor vacuum during post-irradiation anneal, zirconium foil disintegrated.

+ Hardness tests carried out on unirradiated side of specimen.
Table 4

Average Bubble Size Results

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hrs)</th>
<th>Average bubble radius ($\bar{a}$)</th>
<th>Slope of least squares regression line</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>950</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>27</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>35</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>39</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>56</td>
<td>0.19</td>
</tr>
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<td></td>
<td>8</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>1</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>1250</td>
<td>1/2</td>
<td>90</td>
<td>0.19</td>
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<tr>
<td></td>
<td>1</td>
<td>109</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>148</td>
<td></td>
</tr>
<tr>
<td></td>
<td>143</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1350</td>
<td>1</td>
<td>131*</td>
<td></td>
</tr>
<tr>
<td>1450</td>
<td>1</td>
<td>241</td>
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</tr>
</tbody>
</table>

* - too much niobium removed by anodising.
Table 5

Average bubble size/concentration

Heat treatment 1250°C/1 hr

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Concentration (10^{20} \text{ atoms cm}^{-3})</th>
<th>Magnification Plate mag x photo mag</th>
<th>Average bubble diam (Å)</th>
<th>Calculated bubble diam (Å)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H64</td>
<td>1</td>
<td>110K x 4</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>H60</td>
<td>2.5</td>
<td>51.4K x 4</td>
<td>220</td>
<td>204</td>
</tr>
<tr>
<td>H5S</td>
<td>5</td>
<td>51.4K x 4</td>
<td>241</td>
<td>235</td>
</tr>
<tr>
<td>H62</td>
<td>10</td>
<td>51.4K x 4</td>
<td>217</td>
<td>270</td>
</tr>
</tbody>
</table>

* Assuming diam. of 170Å for H64 (10^{20} \text{ atoms cm}^{-3})
Table 6

Bubble mobility for 100Å bubble

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>(D_B) cm(^2) sec(^{-1})</th>
<th>100hr drift distance (\bar{s}) (= (\sqrt{6Dt}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>(1.99 \times 10^{-18})</td>
<td>207</td>
</tr>
<tr>
<td>1250</td>
<td>(1.04 \times 10^{-15})</td>
<td>4740</td>
</tr>
</tbody>
</table>
**Table 7  Disc Electropolishing Conditions**

<table>
<thead>
<tr>
<th>Material</th>
<th>Cathode</th>
<th>Voltage (volts)</th>
<th>Current (mA)</th>
<th>Temperature (°C)</th>
<th>Organic liquid</th>
<th>Head (ins)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium</td>
<td>Pt. wire</td>
<td>14</td>
<td>1</td>
<td>60</td>
<td>dibromoethane</td>
<td>2</td>
<td>Stirrer 100 r.p.m.</td>
</tr>
<tr>
<td>Iron</td>
<td>Pt. wire</td>
<td>25</td>
<td>10-15</td>
<td>20</td>
<td>chloroform</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>