INERT GAS IMPLANTATION OF AMORPHOUS CUZR.

by

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Abstract.

It was proposed that amorphous alloys may be more resistant to radiation damage than crystalline metals. In crystalline metals neutron induced transmutations lead to the formation of inert gas bubbles. These preferentially nucleate near line defects and result in embrittlement. Amorphous alloys do not contain sites where nucleation can occur preferentially.

In this work the growth of argon bubbles in amorphous Cu$_{50}$Zr$_{50}$ has been induced by implanting thin specimens with 80keV argon ions at room temperature. The bubble size distribution was obtained over the dose range $5 \times 10^6$ to $3 \times 10^7$ Ar$^+$ cm$^{-2}$. Larger bubbles grew in the amorphous alloy than would have been expected to grow in a crystalline metal implanted under the same conditions. It was found that ion bombardment caused surface atoms to be sputtered away from the specimens at a rate of 2.3 at. ion$^{-1}$. The sputtering process led to saturation in the amount of argon retained by the material and caused the formation of copper rich near-surface layer. This layer also contained significant amounts of oxygen.

Blister formation was induced at the surface of the amorphous alloy by implanting it with 100keV helium ions. At a critical dose of $3 \times 10^{17}$ He$^+$ cm$^{-2}$ a population of very small blisters was formed. These were the result of large bubbles forming just below the specimen surface. As higher doses were used the features joined up to produce large, thin-lidded blisters at a dose of $10^{18}$ He$^+$ cm$^{-2}$. These observations could not be completely explained in terms of the two popular models of blister formation,
where interbubble fracture or lateral stress result in surface deformation.
Acknowledgements.

I have greatly enjoyed working on this project in the Department of Materials Science and Engineering at the University of Surrey and would like to extend my thanks to all members of the Department for their friendship and support. This project was funded by the SERC to whom I am very grateful. In particular I would like to thank Sarah Clarke for typing much of this manuscript, Fiona Scanlon for typing the equations and Pam Budd and Ray Cox, my office mates, who were a source of valuable discussion.

Special thanks go to Professor Peter Goodhew, who supervised my work with a careful balance of patience, enthusiasm and wit.

Invaluable advice and technical support in the field of electron microscopy was provided by members of the Microstructural Studies Unit: Dawn Chescoe, Vernon Power, Mark Smithers, Gill Gibbs and Jenny Mullervy. In the Department of Electrical and Electronic Engineering I would like to thank the staff of the Ion Implantation Facility along with Chris Jeynes and Roger Webb. I would also like to acknowledge John Evans of AERE Harwell for some useful discussion.

My parents, Derek and Jean, have offered continued support and encouragement in all I have done and this thesis is dedicated to them. Last but not least I would like to pay tribute to the patience of my Fiancée Keri Williams.
The mind of a scholar, if you would have it large and liberal, should come in contact with other minds.

Longfellow - Hyperion.
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1 Introduction.

1.1 Magnetic Fusion and the Demands on Materials.

The topic of magnetic fusion has inspired considerable research interest, and will continue to do so for many years to come. Fusion reactions are potentially a very useful source of energy. Unfortunately the conditions required to induce nuclear fusion are generally detrimental to the integrity of nearby materials. This introduction will outline some of the properties a material would need for use in the containment region of a magnetic fusion reactor, i.e. in the first wall or the superconducting magnets. The success of fusion projects will rely greatly on a drawing together of scientific and engineering disciplines [Krakowski '84]. An important aspect of the fusion reactor program is the need to investigate an ever increasing number of available materials [Nygren '81].

In a magnetic fusion reactor, a plasma of hydrogen isotopes is confined and made to travel along a toroidal path, by magnetic fields. When temperatures in excess of $10^6$K are reached fusion reactions start to take place. The reaction rate per unit volume is given by:

$$\dot{r} = n_1 n_2 \sigma \bar{v} \ldots 1.1$$

where $n_1$ and $n_2$ are the atomic densities of the isotopes involved, $\sigma$ is the reaction cross-section and $\bar{v}$ the average particle
From equation 1.1 the reaction rate per unit volume can be seen to be proportional to $\sigma \nu$. Fig. 1.1 shows the four types of fusion reactions that could be put to use. Although the D-D reactions are favoured by the natural abundance of the isotope in water, the D-T reaction has a more favourable energy yield and a higher rate of reaction. The overall D-T reaction can be written;

$$ ^2_1\text{H} + ^3_1\text{H} \rightarrow ^4_2\text{He} (3.5 \text{ MeV}) + ^1_0\text{n} (14.1 \text{ MeV}) \quad \ldots \ldots 1.2 $$

which is capable of yielding 6MeV per atomic mass unit (amu).

Considerable problems are involved with containing the hot plasma, and dissipating energy from the reactor core. However, the D-T cycle could produce up to 6 times more energy per amu than the conventional fission reaction involving U-235. One difficulty with this cycle is the production of tritium, which is not a naturally occurring isotope. This could be solved by surrounding the plasma with a lithium containing jacket. Neutrons produced in the reactor core would then induce the following reactions;

$$ ^7_3\text{Li} + ^1_0\text{n} \rightarrow ^3_1\text{H} + ^4_2\text{He} + ^1_0\text{n} - 2.87 \text{ MeV} \quad \ldots \ldots 1.3 $$

$$ ^6_3\text{Li} + ^1_0\text{n} \rightarrow ^3_1\text{H} + ^4_2\text{He} + 4.86 \text{ MeV} \quad \ldots \ldots 1.4 $$

Once the D-T cycle has begun, neutrons will be readily available for both tritium production and the removal of energy from the reactor core.

Clearly the high temperatures, along with a flux of high energy neutrons and other particles will be detrimental to the integrity of materials used near the reactor core. It is difficult to estimate the lifetime of a fusion reactor containment system, but the following materials properties must be carefully considered [Megusar et al '81, Kulcinski '78]:

$$ ^7_3\text{Li} + ^1_0\text{n} \rightarrow ^3_1\text{H} + ^4_2\text{He} + ^1_0\text{n} - 2.87 \text{ MeV} \quad \ldots \ldots 1.3 $$

$$ ^6_3\text{Li} + ^1_0\text{n} \rightarrow ^3_1\text{H} + ^4_2\text{He} + 4.86 \text{ MeV} \quad \ldots \ldots 1.4 $$
Fig. 1.1. A comparison of the reaction rates for fusion reactions. $\bar{\sigma}$ is the average over the Maxwellian distribution of cross section times speed, when multiplied by the particle density it gives the fusion rate per unit volume.
(i) Thermal; heat capacity, conductivity, expansivity.

(ii) Mechanical; Young's modulus, yield stress, toughness.

(iii) Electrical; conductivity.

(iv) Nuclear; transmutation reactions, damage per atom, neutron cross-section.

(v) Radiation Effects; swelling, blistering, flaking, sputtering, creep.

The most likely wall materials include austenitic stainless-steels, nickel alloys and refractory metals (V, Nb and Mo) [Ehrlich '77]. However, the investigation of properties for new materials is necessary, as even the prime candidate alloys suffer property degradation in the fusion reactor. Also the conditions to which individual components would be exposed vary greatly with their situation in the reactor; the favourability of a particular material will thus vary with its application. Conditions in a fusion reactor will be more severe than those in a fission reactor because higher energy neutrons will be produced and the structures exposed to radiation will be more complex.

This project is concerned with the fact that materials to be used near the core of a fusion reactor suffer radiation damage. Such damage results from neutron and ion bombardment [Conn '81] which are known to cause two particularly interesting effects in metals:

(i) Atomic displacements.

(ii) Swelling; as a result of inert gas ions being introduced
into the material. Neutrons produced by a fission reaction might be expected to cause 110 displacements per atom (dpa) and produce 1470 atomic parts per million of helium through nuclear transmutations in 10 years of operation at 1MWy⁻² [Mansur '82]. It is well established that the combination of atomic displacements and insoluble helium atoms leads to bubble growth in metals and alloys. This leads to embrittlement, as well as significant swelling and surface flaking. So far all metals have been found to suffer these effects, but the following metallic elements and their alloys have shown some potential as fusion reactor core materials: Ta, W, Cu, Mo, Ti, Al, Nb, Zr, V, Fe.

This document is mainly concerned with the creation of radiation damage, by the implantation of inert gas ions. Such implantations can be used to simulate neutron damage effects, and provide a means of introducing helium (which is produced by neutron induced reactions under reactor conditions). The aim is to investigate the possible resistance of metallic glasses to radiation damage. General information on the nature of metallic glasses (chapter 2) and radiation damage (chapters 3 and 4) is presented and the results of previous experiments involving metallic glasses are reviewed (chapter 5). Later sections of this thesis contain information about experiments performed during the course of the current project.

During the experimental investigations that formed part of this project a CuZr metallic glass was implanted with argon, krypton and
helium ions. Analytical techniques were used to study the surface erosion and microstructural changes induced by the heavier ions. Helium implantations resulted in the development of surface blisters and flakes.

1.2 The Possible Resistance to Radiation Damage of Metallic Glasses

Metallic glass phases can be produced by solidifying certain alloys at high cooling rates. For crystalline alloys, it is well known that changing the rate of solidification imposed during alloy production, provides a means of controlling the microstructural development. As a result some control over the properties related to microstructure can be achieved. By way of an example, we can consider the case of alloys which possess second phase particles in their microstructure; because such particles act as nucleation sites for inert gas bubbles. Rapid solidification provides a means of obtaining an even distribution of small particles and hence of bubbles. This results in lower levels of radiation induced embrittlement. The effect of precipitate refinement has been studied by Grant et al ['81] and Imeson et al ['81].

In general microstructural features become finer and more homogeneous, as the rate of alloy solidification is increased. It is also possible to increase the solid solubility of phases [Luborsky '83]. At high cooling rates (>10⁶Ks⁻¹), and for certain alloys, the liquid to solid phase change becomes a second order transition and solidification produces a metallic glass.
These materials exhibit short range atomic order, but lack long range atomic order. The first examples were produced by Duwez et al in 1967 [Duwez '67].

The properties of metallic glasses have sometimes proved surprising, for example; some have a negative thermal coefficient of resistivity. A completely satisfactory model of their atomic and electronic structures has yet to be developed.

It is important when considering this work to note that metallic glasses are free of crystal defects (e.g. grain boundaries and dislocations) and rarely contain precipitate particles. The existence of such defect structures is known to aid the growth of inert gas bubbles in crystalline metals. The absence of defects suggests that bubble nucleation will occur homogeneously, and leads to the proposal that metallic glasses may be less susceptible to swelling in a fusion reactor environment than conventional alloys [Megusar et al '81]. Metallic glasses are structurally quite different from crystalline alloys, so radiation damage in them is likely to occur via novel mechanisms. However, no definitive structural model is available for metallic glasses, so it is difficult to describe (intrinsic or extrinsic) defects. Further even for crystalline metals the behaviour of radiation induced defects must be inferred from observations made late in the development of a damaged microstructure (e.g. after gas bubble formation). As a result there is always likely to be some doubt as to how these defects behave. For metallic glasses the uncertainties of defect structure and their subsequent behaviour are compounded when radiation induced microstructural changes occur. During later
discussion of the mechanisms for microstructural development in crystalline metals this problem will become clear. Quantitative modelling of radiation damage effects often demands that informed assumptions are made about defect behaviour; this is particularly true in the case of metallic glasses. It is difficult to produce an equation describing the movement of a defect, when the structural nature of that defect is unknown.
2 Metallic Glasses

2.1 Introduction

A glass is defined as a solid produced by continuous cooling of a melt, such that detectable crystallisation is avoided. Major reviews of the formation and properties of metallic glasses have been published by Cahn ['80] and Chen ['80]. Alloys which form metallic glasses are usually found to have a relatively small difference in free energy between their liquid and equilibrium crystalline states. Such alloys can be made to form a glass by several techniques, one of which is termed "splat quenching".

Splat quenching itself takes many forms, the most popular of which is melt spinning. During this process a molten alloy is directed onto a cold copper roller rotating at high speed. Fig.2.1 shows schematically how a melt puddle forms on the roller and how a thin ribbon of rapidly quenched metal is drawn from it. Important process parameters are: 1, the length of the melt puddle, w, the angular velocity of the roller and $\alpha$, the inclination of the melt jet with respect to normal incidence to the roller. The relation of these and other factors to the cooling rate achieved, and the dimensions of the final product have been studied by several research groups (e.g. Budhani et al ['82], Davies ['83], Anthony and Cline ['79] and Lieberman ['81]).
Fig. 2.1. A schematic diagram of the melt spinning process.
Other processes by which metallic glass formation can be achieved include: sputter or vapour deposition, laser quenching, chemical deposition, ion bombardment (which will be discussed further in section 5.2) and solid state reaction.

The glassy state is generally metastable and can be attained by solidifying the alloy at such a rate that the formation of crystals is kinetically inhibited. That is, if the viscosity of the melt is forced to rise rapidly enough, atomic mobility is reduced and the long range diffusion required to grow crystals is prevented. The atomic structure of amorphous alloys will be discussed later in this chapter.

A glass is usually defined as having formed when the viscosity of the melt exceeds $10^{13}$ poise. The temperature at which this viscosity is reached is termed the glass transition temperature, $T_g$ (see fig.2.2). $T_g$ is usually measured with a differential scanning calorimeter, which charts the specific heat capacity of the glass. Fig.2.3 shows how the enthalpy and specific heat capacity are thought to change during glass formation. For comparative purposes the changes in these properties during crystallisation are also shown (fig.2.3).

The techniques used for metallic glass production do not lend themselves to the measurement of $T_g$ during solidification, mainly because the quench rates are so high. However, Nishi et al ['81a and b] have made some effort in this direction.

Theoretically it should be possible to quench any metallic melt
Fig. 2.2. Viscosity ($\eta$) - temperature ($T$) behaviour corresponding to crystallisation and vitrification of a metallic melt.

Fig. 2.3. The temperature dependence of the enthalpy ($H$) and specific heat ($C_p$) corresponding to crystallisation and vitrification of a metallic melt.
such that a metallic glass forms. However, present quenching techniques are only capable of providing cooling rates up to \( \sim 10^7 \text{Ks}^{-1} \). This has proved sufficient for the production of a huge number of metallic glasses [Jones and Suryanarayana '73]. It is recognised that pure metals do not form glasses as a result of cooling at these rates and that certain types of alloy composition are favoured. The following factors contribute to an alloy being a good glass former:

(i) The addition of solute atoms increases the probability that ordering will be kinetically inhibited by quenching. The introduction of atoms of significantly different size to the host atoms makes atomic rearrangements more difficult and so increases the likelihood of retaining a random structure after solidification. The alloy is also more likely to be a good glass former if the solute atoms introduce some amount of bond directionality.

(ii) Alloying also increases the thermodynamic stability of the amorphous phase. This is demonstrated by a reduction in the equilibrium freezing temperature \( T_1 \) (the liquidus temperature) and an increase in the glass transition temperature, \( T_g \). As a result the temperature difference through which the melt must be cooled to prevent crystallisation is reduced, making the required rate of cooling more easily achieved.

(iii) The smallest difference between \( T_1 \) and \( T_g \) usually occurs in the region of deep eutectic compositions [Boettinger '81, Massalski '81].

(iv) Wide glass forming ranges are often associated with alloys
which exhibit extended eutectics. Such ranges are generally the result of one or more interstitial phases of relatively low stability.

Although several subclasses of glass forming alloys have been identified [Jones '83], they can be divided into two main types:

(i) Transition metal-metalloid alloys (TM-M), which usually exhibit a narrow composition range of good glass forming ability, centred on a 13-25 at% metalloid eutectic. Examples are PdSi, FeB.

(ii) Early transition metal-late transition metal alloys (TM-TM), which usually exhibit a wide eutectic region as described in (iv) above. Examples are CuTi, CuZr, NiZr, NiNb. These alloys often form glasses with a higher crystallisation temperature than TM-M glasses.

TM-M glasses are not suitable for applications where they might be subjected to a flux of neutrons, as metalloid atoms have a relatively high interaction cross section for neutrons. For this reason a TM-TM glass was chosen for this project.

It should be noted that $T_g$ and the atomic structure of metallic glasses are affected by the cooling rate imposed during production. This is schematically demonstrated in fig.2.4 where fast cooling can be seen to produce a higher $T_g$, and a higher specific volume, than slow cooling. For metallic glasses the
Fig. 2.4. Schematic diagram of the changes of specific volume of a liquid with temperature by fast and slow cooling.
possible effects of different cooling rates should be borne in mind. This is particularly true when considering alloys produced by different techniques. For example, sputter deposition is expected to achieve a higher effective cooling rate than splat quenching, so sputter deposited alloys contain more free volume than splat quenched ones [Rivory et al '82]. By contrast solid state reactions produce an amorphous phase very slowly. As a result, these reactions are expected to give a structure with relatively little free volume. Solid state amorphisation demonstrates that some amorphous phases are extremely stable with respect to their crystalline counterparts [Schwarz et al '84, Schwarz and Johnson '83 and Atzmon et al '84].

2.2 The Atomic Structure of Metallic Glasses

Insight into the differences in atomic structure between crystalline and amorphous metals is most readily gained by reviewing neutron, X-ray or electron scattering studies. X-ray diffraction is the most widely used of these techniques. For a polycrystalline sample X-rays are diffracted into strong peaks when they meet an atomic plane and satisfy the well known Bragg condition;

\[ n\lambda = 2d\sin\theta \]  

However, atoms in an amorphous alloy do not form planar arrays. As a result scattering is diffuse in these materials and a series of peaks of relatively low intensity are observed, as shown in fig.2.5. Maxima occur in the scattered intensity, which correspond to the average first, second, third..... nearest neighbour atomic
Fig. 2.5. Diffuse intensity obtained by X-ray scattering from several amorphous CuZr alloys.
separations. The diffuse nature of these peaks emphasises the fact that throughout the metal atoms are separated by a range of distances. Diffraction patterns from amorphous alloys bear close resemblance to patterns obtained from liquids. Diffraction patterns are normalised and plotted against, \( k = 4\pi \sin \theta / \lambda \), instead of \( 2\theta \) (see fig.2.5). The application of a Fourier transform allows an atomic radial distribution function or RDF \( \sigma(r) \) to be calculated. \( \sigma(r) \) is such that the number of atoms to be found in a spherical shell between distances \( r_1 \) and \( r_2 \) from a central atom can be estimated using the integral:

\[
\int_{r_1}^{r_2} 4\pi r^2 \sigma(r) \, dr
\]

An example of an RDF is displayed in fig.2.6. The important components of the distribution are peaks corresponding to the first, second, and third nearest neighbours. Anomalous peaks to the left of the first coordination peak are the result of truncating the fourier transform (i.e. not being able to integrate to \( \infty \)).

More detailed information can be obtained from some amorphous alloy systems. RDF's can be further treated to reveal partial RDF's which correspond to the separation of the possible atom pairs, i.e. in a binary system the length of A-A, B-B, and A-B bonds. Partial RDF's are described in several review articles, for example Lele ['84], Wagner ['83] and ['80], Cahn ['80], Sakata et al ['81]. Unfortunately their usefulness is not universal for metallic glass, because the resolution that can be achieved requires the alloy components to scatter incoming waves with quite different efficiencies. Copper and zirconium form one system for which the deconvolution of partial RDF's is particularly difficult [Sakata'81].
Fig. 2.6. The radial distribution functions obtained from fig. 2.5.
To understand the atomic structure of amorphous alloys model structures are produced and the theoretical RDF's are compared with the experimental ones. The earliest examples of this type of investigation were based on physical models and performed by Bernal [’60 & ’64] and Scott [’60]. Originally this type of approach, which is termed the dense random packing of hard spheres (DRPHS), was applied to simple liquids. It was later developed for solid amorphous metals by Finney [’70, ’70,] and Finney and Wallace [’81]. The advent of computer simulations allowed RDF's to be calculated rapidly and with a variety of interatomic potentials. The use of relaxed potentials led to the DRP of soft sphere (DRPSS) models. Fig. 2.7 shows a comparison of Finney's DRPHS model with experimental evidence for Ni$_{76}$P$_{24}$. The agreement is reasonably good. However, the model RDF was produced only using spheres corresponding to nickel atoms. No account was taken of phosphorous atoms being present. During these studies the density of the model was calculated and expressed in terms of a packing fraction, the fraction of space occupied by spheres was ~0.63%. This value is nearly 10% lower than that estimated for the actual glass. A paper of import to the understanding of atomic structure in TM-M glasses was published by Polk [’72]. In this paper it was suggested that the metalloid atoms would reside interstitially, at the centre of holes known as "Bernal polyhedra". These holes are characteristic of the DRPHS structure. Ahmadzadeh and Cantor [’81] presented the diagrams contained in fig. 2.8 which depict the largest of these Bernal polyhedra. They also presented a review of several DRPHS and DRPSS models. Table 2.1 is a summary of the number of these Bernal polyhedra which can be attributed to any one atom. The volume percentages occupied by the principal polyhedra are given in
Fig. 2.7. Comparison between the radial distribution function of Finney's DRPHS structure (histogram) and amorphous Ni$^{76}P_{24}$.

Fig. 2.8. Bernal's canonical holes.
<table>
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<tr>
<th>Reference Model</th>
<th>Bonding distance</th>
<th>Bernal</th>
<th>Whittaker</th>
<th>Frost</th>
<th>Frost</th>
<th>Frost</th>
<th>Frost</th>
</tr>
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<tr>
<td>Tetrahedra</td>
<td>~1.4</td>
<td>1.4</td>
<td>1.2</td>
<td>1.2</td>
<td>1.3</td>
<td>1.2</td>
<td>1.3</td>
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<tr>
<td>Octahedron</td>
<td>0.224</td>
<td>0.07</td>
<td>0.01</td>
<td>0.107</td>
<td>0.010</td>
<td>0.249</td>
<td>0.011</td>
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<td>0.002</td>
<td>0.015</td>
<td>0.003</td>
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<td>Tetragonal dodecahedra</td>
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<td>0.143</td>
<td>0.03</td>
<td>0.045</td>
<td>0.007</td>
<td>0.077</td>
<td>0.006</td>
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<tr>
<td>Trigonal prism + 1/2 oct. caps</td>
<td></td>
<td>0.148</td>
<td>0.003</td>
<td>0.002</td>
<td>0.025</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>Archimedean antiprism + 1/2 oct. caps</td>
<td></td>
<td>0.018</td>
<td>0.007</td>
<td>0.003</td>
<td>0.017</td>
<td>0.003</td>
<td>0.006</td>
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<tr>
<td>Deltahedra with 16/18 faces</td>
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<td>0.015</td>
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<td>0.026</td>
<td>0.005</td>
<td>0.006</td>
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<td>(2) Other polyhedra</td>
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<td></td>
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<tr>
<td>Half octahedron (all)</td>
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<td>0.939</td>
<td>0.65</td>
<td>0.856</td>
<td>1.006</td>
<td>0.709</td>
<td>0.979</td>
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<td>Half octahedron (isolated)</td>
<td></td>
<td>0.27</td>
<td>0.02</td>
<td>0.273</td>
<td>0.017</td>
<td>0.184</td>
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<td>0.02</td>
<td>0.127</td>
<td>0.011</td>
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<td>0.010</td>
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<td></td>
<td>0.018</td>
<td>0.002</td>
<td>0.004</td>
<td>0.007</td>
<td>0.004</td>
<td>0.001</td>
</tr>
<tr>
<td>Half dodecahedra</td>
<td></td>
<td>0.24</td>
<td>0.02</td>
<td>0.236</td>
<td>0.142</td>
<td>0.222</td>
<td>0.210</td>
</tr>
<tr>
<td>(3) Other shapes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dihedron (all)</td>
<td></td>
<td>1.04</td>
<td>0.98</td>
<td>0.571</td>
<td>1.156</td>
<td>0.722</td>
<td></td>
</tr>
<tr>
<td>Dihedron (isolated)</td>
<td></td>
<td>0.80</td>
<td>0.03</td>
<td>0.589</td>
<td>0.25</td>
<td>0.2</td>
<td>0.834</td>
</tr>
<tr>
<td>Pentatope</td>
<td></td>
<td>0.05</td>
<td>0.01</td>
<td>0.097</td>
<td>0.010</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>7 point bisymmetric</td>
<td></td>
<td>0.013</td>
<td>0.004</td>
<td>0.004</td>
<td>0.001</td>
<td>0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>7 point trisymmetric</td>
<td></td>
<td>0.04</td>
<td>0.01</td>
<td>0.032</td>
<td>0.006</td>
<td>0.016</td>
<td>0.006</td>
</tr>
<tr>
<td>Mutated archimedean antiprisms</td>
<td></td>
<td>0.10</td>
<td>0.09</td>
<td>0.010</td>
<td>0.005</td>
<td>0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>Shapes with &gt;8 vertices</td>
<td></td>
<td>0.061</td>
<td>0.006</td>
<td>0.019</td>
<td>0.004</td>
<td>0.024</td>
<td>0.007</td>
</tr>
</tbody>
</table>
The largest polyhedra are thought to be capable of accommodating ~20% of the metalloid atoms; this leads to a more realistic density for the model structure.

From the densities, the size of the TM atoms and crystalline information appropriate to a particular amorphous alloy it is possible to estimate the size of metalloid atoms within that alloy ($r_M$) [Turnbull '77]. If this is repeated for a number of TM-M glasses $r_M$ is found to be a variable which depends on the type of TM atoms involved. Turnbull suggested that the TM-M interaction is the result of a relatively soft potential, so the presence of metalloid atoms does not cause the TM atom positions to differ greatly from those suggested by the DRPHS models. Direct evidence that TM-M glasses are based on a DRPHS array is provided by partial RDF's. These suggest that M-M bonds are unfavoured in the alloy, i.e. that considerable compositional short range order (CSRO) exists [Egami '83, Suzuki '83, Takayama '76, Warlimont '84]. In TM-TM glasses for which partial RDF's can be obtained there is little evidence of CSRO. It seems probable that each type of atom present resides on sites of the DRPHS structure.

2.3 Studies of Atomic Structure in Amorphous CuZr Alloys

As mentioned in the previous section the study of CuZr amorphous alloys by the most popular scattering technique, X-ray diffraction, is not very fruitful because copper and zirconium atoms have similar scattering factors. Despite this fact Dargel-Sulir et al ['82]...
Volume percentages occupied by polyhedra in DRPHS models (see Ahmadzadeh and Cantor '81).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Bernal</th>
<th>Frost</th>
<th>Frost</th>
<th>Frost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>Bernal</td>
<td>Finney</td>
<td>Finney</td>
<td>Bennett</td>
</tr>
<tr>
<td>Bonding distance</td>
<td>~1.4</td>
<td>1.2</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>48.4</td>
<td>19.01</td>
<td>40.24</td>
<td>13.71</td>
</tr>
<tr>
<td>Octahedron</td>
<td>12.86</td>
<td>6.66</td>
<td>15.77</td>
<td>2.71</td>
</tr>
<tr>
<td>Pentagonal bipyramid</td>
<td>0.29</td>
<td>1.34</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Tetragonal dodecahedra</td>
<td>14.8</td>
<td>5.15</td>
<td>9.14</td>
<td>2.83</td>
</tr>
<tr>
<td>Trigonal prisms with caps</td>
<td>20.52</td>
<td>0.49</td>
<td>3.75</td>
<td>0.56</td>
</tr>
<tr>
<td>Archimedean antiprism with caps</td>
<td>3.16</td>
<td>1.21</td>
<td>3.03</td>
<td>0.92</td>
</tr>
<tr>
<td>Deltahedra with &gt;16 faces [a]</td>
<td>67.19</td>
<td>26.73</td>
<td>79.06</td>
<td></td>
</tr>
</tbody>
</table>
produced RDF's from X-ray diffraction studies of amorphous 
$\text{Cu}_x\text{Zr}_{100-x}$ (for $x = 40, 45, 50, 60$). The position of the first 
and second peaks in these patterns (with the second peak slightly 
split to give $r_2$ & $r_2'$) are shown in table 2.3. The 
position of the peaks were found to be similar to those in liquid 
copper and zirconium. The position of the first peak moves 
noticeably to smaller values of $r$ as the copper content increases.

Sadoc et al ['84] applied extended X-ray absorption fine 
structure analysis in an attempt to study the atomic structure of 
$\text{Cu}_x\text{Zr}_{100-x}$ glasses (for $x = 33, 46, 60$). With this technique 
partial RDF's are obtained from the characteristic edges for $\text{Cu}_K$ and $\text{Zr}_K$ excitations. A strong similarity was found between 
local atomic arrangements in the amorphous alloys and crystalline $\text{Cu}_{10}\text{Zr}_7$.

In his review on metallic glasses Chen ['80] presented 
conclusions reached by Mizogetcic et al after X-ray diffraction 
 studies. These studies involved a variety of Zr-TM glasses. For 
some of the alloys partial RDF's were calculated. It was discovered 
that the intensity of the first and second peaks in the Zr-TM RDF's 
was sharper than those of the Zr-Zr or TM-TM distributions. The 
Zr-TM interactions exhibited more tightly defined separations, and 
so indicated that the corresponding bonds were preferred.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_3$</th>
<th>$r_2/r_1$</th>
<th>$r_3/r_1$</th>
<th>$r_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{40}$Zr$</em>{60}$</td>
<td>3.15</td>
<td>5.35</td>
<td>5.95</td>
<td>1.71</td>
<td>1.89</td>
<td>7.50</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$</td>
<td>3.04</td>
<td>5.48</td>
<td>5.68</td>
<td>1.70</td>
<td>1.87</td>
<td>7.75</td>
</tr>
<tr>
<td>Cu$<em>{30}$Zr$</em>{70}$</td>
<td>2.85</td>
<td>4.94</td>
<td>5.37</td>
<td>1.69</td>
<td>1.88</td>
<td>7.40</td>
</tr>
<tr>
<td>Cu$<em>{60}$Zr$</em>{40}$</td>
<td>2.80</td>
<td>4.84</td>
<td>5.41</td>
<td>1.72</td>
<td>1.93</td>
<td>7.05</td>
</tr>
<tr>
<td>Liquid Cu (1150°C)</td>
<td>2.57</td>
<td>4.75</td>
<td>1.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid Zr (1900°C)</td>
<td>3.19</td>
<td>6.02</td>
<td>1.89</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Defects in amorphous alloys are readily described by their geometric deviation from the homogeneous matrix. Well known examples are contained in the table below:

### Table 2.4.

<table>
<thead>
<tr>
<th>Point Defects</th>
<th>Chemical Impurities</th>
<th>Extended Defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancies</td>
<td>Substitutional</td>
<td>Dislocations</td>
</tr>
<tr>
<td>Interstitials</td>
<td>Interstitial</td>
<td>Stacking faults</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Precipitates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Grain boundaries</td>
</tr>
</tbody>
</table>

For amorphous solids the definition of an ideal reference structure is not so clear. Further, defects (deviations from the ideal structure) are diffuse, i.e. involve a collection of atoms. In general the presence of defects is detected by comparing experimental observations with parameters obtained by computer calculation [Popescu '84].

For organic silicate-type, and perhaps TM-M glasses, network structures based on compositional SRO may be used as models. This allows the following point defects to be defined: (a) dangling bonds, (b) wrong bonds, (c) valence alternation pairs, (d) atoms with low stress fields (quasi vacancies) and (e) atoms with high stress fields (quasi-interstitials). The extended defects (d) and (e) may be termed quasi-vacancy or quasi-interstitial dislocations. It may also be possible that domain boundaries exist between different amorphous phases in a sample. Defects may also be
described as intrinsic (i.e. they are characteristic of the material after relaxation) and extrinsic (i.e. they annihilate during relaxation.)

Several attempts have been made to model the behaviour of vacancy type defects in metallic glasses [Popescu '84, Spaepen '78, Bennett '72 and Bennett et al '79]. In general it is agreed that the removal of an atom from a DRPHS structure leads to an unstable situation. Such quasi-vacancy defects are thought to collapse, even when the material is well below room temperature. Fig.2.9 shows a sequence illustrating the collapse of a vacancy in a two-dimensional dynamic hard sphere model [Popescu '84]. During the rapid solidification of molten alloys to form glasses some of the free volume associated with the liquid state is conserved. It has been suggested that such free volume becomes mobile just below $T_g$ and that it will migrate towards free surfaces. As a result a more relaxed structure, close to the "ideal glass structure" is produced. [Goudeau et al '84, Inoue et al '84 and '85].

Some attempts have been made to model the results of ion implantation experiments on metallic glasses [Doyama '81, Krishan '82]. These were mainly concerned with the formation of cascades. So far no efforts have been made to evaluate the stability of defects produced in metallic glasses by implantation.
Fig. 2.9. The collapse of a quasi-vacancy in a two-dimensional hard sphere experiment: (a) initial random structure, (b) shaded atom removed, (c) start of collapse, (d) quasi-vacancy disappears.
2.5 Crystallisation

2.5.1 Of Metallic Glasses in General.

A commonly used method of displaying the route to amorphisation, and the subsequent possible crystallisation products is the Time-Temperature-Transformation (T-T-T) diagram. The T-T-T curve for a particular crystalline phase is derived from the Johnson-Mehl-Avrami treatment of transformation kinetics (as utilised by Uhlman ['72 and '78] and Davies et al ['74]), with the fraction of transformed phase produced in a time $t$ being given by;

$$x \sim \pi v^3 t^{4/3}, \text{ for small } x$$

where the crystal growth rate $u$ is;

$$u = f v_a \left[ 1 - \exp\left(\frac{-\Delta H_f \Delta T_r}{RT}\right)\right]$$

$f$ is the fraction of surface sites capable of accepting atoms (-1 for close packed crystals and 0.2 $T_r$ for faceted crystals), $a_0$ is the mean atomic diameter. $I_v$ is the homogenous nucleation frequency, $\Delta H_f$ is the molar enthalpy of fusion, $\Delta T_r = (T_1 - T)/T_1$ the reduced undercooling, $v_\phi$ is the kinetic transport coefficient at the crystal-liquid interface (taken by Uhlman to be the Stokes-Einstein coefficient $v_\phi = k_B T / 6 \pi \eta a_0^3$, $\eta$ being the viscosity). In addition the nucleation frequency can be expressed as [Uhlman '72];

$$I_v = N v g \exp\left(-1.024/T_r^3 \Delta T_r^2\right)$$

where $N$ is the number of atoms per unit volume.
Generally equation 2.2 is used to calculate the time taken for a given fraction of crystalline metal to form, as shown in fig.2.10. The cooling rate required to avoid crystallisation is then estimated from the position of the 'nose' of the T-T-T curve. That is using:

$$\frac{dT}{dt} = \frac{\Delta T_n}{t_n}$$

Where $T_n = T_1 - T_n$, with $T_n$ being the temperature at the nose of the curve, and $t_n$ being the time coordinate of the nose of the curve (see fig.2.10).

Crystallisation of a glass can take place as a result of isothermal annealing in a finite crystallisation time. It can also be induced by continuous heating, which leads to a measurable crystallisation temperature. A large number of experiments have been carried out to measure crystallisation temperatures, usually through DSC or resistivity measurements [Scott '83]. It should be noted when using reported values of crystallisation temperatures that the results are sensitive to the rate of heating.

The products of crystallisation can also be affected by heating rate, as fig.2.11 demonstrates schematically. Two crystalline products are possible in this diagram and kinetic factors have an influence on the phase produced. The expected products of crystallisation can be inferred from free energy diagrams like fig.2.12. The possible modes of crystallisation demonstrated by this figure are:

(i) Polymorphous crystallisation modes; (1) to the stable
Fig. 2.1. A schematic T-T-T diagram for crystal growth in an under-cooled melt: (a) fast cooling to form glass, (b) isothermal heating to crystallise glass at time $t_x$, (c) slow heating of the glass to produce crystallisation at $T_x$.

Fig. 2.11. A T-T-T diagram with two possible products of crystallisation: (a) rapid quenching leads to glass formation avoiding the crystallisation of $a$ and $B$, (b) heat treatment of the glass generally produces the metastable crystalline phase $B$. 
Fig. 2.12. Hypothetical free energy diagram illustrating the crystallisation of a metallic glass. G, α, θ, M are respectively the free energy curves of the glass, a terminal solid solution, a stable intermetallic phase and a metastable phase. Stable equilibrium is indicated by the solid line; metastable equilibrium by the dotted lines. The arrows indicate possible devitrification processes.
intermetallic phase. (2) to a metastable phase \( m \) and (3) to a supersaturated solid solution. Modes (2) and (3) may subsequently lead to (2') and (3') which result in the equilibrium mixture of \( \Theta \) and \( \alpha \).

(ii) Eutectic crystallisation; where the composition of the glass leads to (4)\( \alpha \) and \( \Theta \) or (5)\( \alpha \) and \( m \).

(iii) Primary Crystallisation; (6) formation of the supersaturated solid solution. An enriched glass will be formed between crystallites of \( \alpha \) and due to solute rejection. This glass will then decompose by modes (i) or (ii) above.

In general the final products of crystallisation for a metallic glass are the equilibrium phases. On the way to these products, a number of metastable phases may be formed. This is in agreement with Ostwald's rule [Auseau '73].

2.5.2 The Crystallisation of CuZr

The copper-zirconium system was one of the first TM-TM alloys to exhibit full amorphisation. The composition found to be most easily produced in the amorphous state by rapid solidification was \( \text{Cu}_{60}\text{Zr}_{40} \). To date however, there have been a large number of different amorphous phases produced. Fig.2.13 is a diagram schematically presenting the phase diagram of CuZr, it displays the range of compositions over which amorphous phases have been produced. The figure also contains the glass forming
Fig. 2.13. Schematic phase diagram including the experimentally determined glass forming range and the calculated range obtained by Saunders and Miodownik ['86].
range predicted by Saunders and Miodownik ['86]. Atzmon et al ['84] succeeded in producing significant amounts of amorphous CuZr by diffusion in the solid state. This emphasises the relatively high stability of the amorphous state in the CuZr system. An early phase diagram of the CuZr system is contained in fig. 2.14, after Lundin et al ['53]. A more recent version was prepared by Lou and Grant ['84], as shown in fig. 2.15. The most recent investigation of this system was performed by Kneller et al ['86]. The most notable difference between the two diagrams lies at the composition Cu\textsubscript{14}Zr\textsubscript{7}, where an intermetallic phase has been discovered. This phase was first identified by Bsenko ['75]; verifications of its existence have come from Vitek et al ['75] and Marshall et al ['81]. The original identification was made with the aid of isomorphous Ni\textsubscript{10}Zr\textsubscript{7} [Kirkpatrick et al '62]. The space group for both Ni\textsubscript{10}Zr\textsubscript{7} and Cu\textsubscript{14}Zr\textsubscript{7} is C2ca, and the lattice parameters for Cu\textsubscript{14}Zr\textsubscript{7} are: a=12.673, b=9.316, c=9.347 [Bsenko '75].

Several studies of the crystallisation kinetics of CuZr metallic glasses have been published. The most important for this particular thesis are those concerned with alloys close to the composition Cu\textsubscript{50}Zr\textsubscript{50}. Calvayrac et al ['80] compared the thermal behaviour of twin roller quenched and melt spun Cu\textsubscript{60}Zr\textsubscript{40}. Table 2.5 shows values of the glass formation temperature (T\textsubscript{g}), crystallisation temperature (T\textsubscript{c}) and heat of crystallisation (\Delta H\textsubscript{c}) that were obtained.
Fig. 2.14. The CuZr phase diagram from 1953.

Fig. 2.15. The revised CuZr phase diagram.
Table 2.5.

<table>
<thead>
<tr>
<th></th>
<th>Twin roller quenched</th>
<th>Melt spun.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (K)</td>
<td>701</td>
<td>701</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>745</td>
<td>750</td>
</tr>
<tr>
<td>$\Delta H_c$ (KJmol$^{-1}$)</td>
<td>4</td>
<td>4.2</td>
</tr>
</tbody>
</table>

The behaviour of both types of specimen was similar, however the results from melt-spun specimens displayed a greater scatter suggesting a less uniform cooling rate during solidification. Several effects associated with oxidation were noted:

(i) When stored under ambient conditions for a few days the surface of specimens was seen to change colour (a copper-like hue was observed during this project).

(ii) Annealing well above $T_g$ encouraged the formation of copper and monoclinic zirconia; this was revealed by X-ray diffraction. The Bragg reflections associated with their presence could be removed by mechanically polishing the specimen surface.

(iii) In the TEM thin specimens of amorphous metals exhibited interesting edge effects. That is, the structure was different near the edge. Electron diffraction patterns revealed this difference, the diffuse ring associated with the metallic glass was seen to split into two diffuse rings as the beam was moved towards the hole. One of the rings lay in the position of that present when thicker regions were examined, while the second indicated the existence of an amorphous material for which the average
atomic separation was greater than that of the bulk.

Each of the effects noted above were found to occur during the course of this project.

The third observation listed above was also made by Vitek et al ['75], during studies in which the metallic glass was heated in the TEM. Vitek concluded that a "transformed amorphous phase" had been produced. Later Calvayrac pointed out that this phase was probably the result of oxidation at the specimen surface. This only becomes clear near the edges of holes in the specimens where the amount of unoxidised metal is lowest. A detailed analysis of oxidation at the surface of CuZr TEM specimens, before and after ion implantation, was performed in this project. The results will be displayed in chapter 7.

The presence of oxygen in metallic glasses is extremely difficult to avoid, because the constituent elements are often quite reactive. For example, zirconium has a high affinity for oxygen. According to Aoki et al ['86] the presence of oxygen does not necessarily affect the bulk behaviour of a glass. His studies involved the crystallisation of amorphous NiZr; the formation of ZrO$\text{_{2}}$ and Ni$_{10}$Zr$_{7}$ were noted. The Ni$_{10}$Zr$_{7}$ phase was expected without the presence of oxygen. Marshall studied the crystallisation of Cu$_{60}$Zr$_{40}$ in the TEM and recorded the formation of Cu$_{10}$Zr$_{7}$, despite the fact that heating of thin films in the TEM is known to cause oxidation [Calvayrac et al '80]. Similar results were obtained by Chevalier et al ['83] for Cu$_{60}$Zr$_{40}$ doped with 0.5 at%
oxygen, in this case diffraction revealed the presence of 
\( \text{Cu}_{4}Zr_{7} \) and monoclinic \( ZrO_{2} \). Despite these 
observations several investigators have shown that the presence 
of small amounts of oxygen distributed through the metallic glass 
does affect its thermal behaviour. As a result the presence of 
oxygen can be detected by differential scanning calorimetry (DSC) 
[Polk et al '78]. Fig.2.16 contains DSC traces which indicate 
some difference in thermal behaviour between metallic glasses 
prepared without oxygen and those with oxygen introduced.

Having implied that the presence of oxygen is virtually 
unavoidable (at least on the surface of the specimen) for 
zirconium compounds, a brief review of oxidation studies 
performed on zirconium and CuZr alloys will now follow.

2.6 Oxidation of Zirconium and CuZr Alloys

The solubility of oxygen in zirconium has been studied by many 
workers, and reviews of papers dealing with this topic exist in 
books written by Douglass ['71], and Kofstad ['66]. It is known 
that the affinity of zirconium for oxygen is high. For this thesis 
the most relevant observations on the nature of oxidation of 
zirconium were made by Ploc ['68] and Douglass and Van Landuyt ['65] 
who separately observed significant quantities of amorphous or 
pseudo-amorphous surface oxide on their specimens. Unfortunately no 
quantitative analysis was performed on their electron diffraction 
patterns, so comparison with diffraction patterns recorded during
Fig. 2.16. Thermograms showing the variation in behaviour with oxygen content for the amorphous CuZr alloy. The upper set of traces were recorded at 1/5 the sensitivity of the lower set.
the course of this project is not possible. However, split amorphous rings have been observed in this work and in the work of others (as mentioned in the previous section). The inner rings are probably attributable to the presence of amorphous zirconia at the surface of the specimens.

A number of oxidation experiments have been performed on crystalline CuZr alloys. The addition of small quantities of transition metal atoms to zirconium has been used to impede oxidation, through the formation of intermetallics which oxidise preferentially. However, CuZr alloys generally oxidise more rapidly than pure zirconium. Fig. 2.17 shows schematically what happens when the alloys oxidise. Very few copper atoms enter the surface oxide film instead crystals rich in copper precipitate below a layer of zirconia [Kondo and Kimura '71].

Bigot et al ['81] studied the weight gain of amorphous Cu_{60}Zr_{40}, as a result of oxygen take-up. Their observations showed that more oxygen was taken up under lower partial pressures. Their conclusion was that exposure to a high partial pressure of oxygen allowed a layer of zirconia to form rapidly at the specimen surface, this layer then provided a barrier to further oxidation. Confirmation of this conclusion is provided by an electron spectroscopic study of the surface oxidation of amorphous and crystalline alloys, performed by Sen et al ['84]. Their results reveal the formation of layers of zirconia at the surface of both types of specimen during oxidation.
Fig. 2.17. A schematic diagram showing the results of oxidising a NiZr alloy. Similar layers are expected to occur for CuZr.
2.7 Diffusion in Amorphous Alloys

An understanding of diffusion processes in amorphous alloys is important as many of the unusual properties they possess depend on atomic movement. Examples of such properties are:

(i) Crystallisation [Davies '76].

(ii) Structural relaxation (leading to reversible and irreversible changes in physical behaviour through changes in the amount of short range order present in the material [Egami '83]).

A review which deals particularly well with the effects of diffusion on the properties of metallic glasses has been written by Chen ['83]. Examples of experimental diffusion studies, with particular relevance to the CuZr system, have been published by Drijver et al ['81], Goudeau et al ['84], Chen ['78] and ['81], Kijek ['80] and Zielinski ['78].

Diffusion is an important aspect of projects dealing with the formation of inert gas bubbles, as bubble nucleation and the mechanisms of growth depend on the mobility of both gas and metal atoms (see chapter 3). A comprehensive review of diffusion data for amorphous alloys has been produced by Cantor and Cahn ['83]. Their display of data, reproduced in fig.2.18, shows that the results of all the experiments included fall between data for boron diffusing in fcc iron and gold diffusing in fcc nickel. These particular lines are useful for reference purposes as they respectively represent interstitial and substitutional diffusion processes.
Fig. 2.18. Diffusion data collated by Cantor and Cahn [ '83].

Fig. 2.19. Normalised Arrhenius plots for TM-M glasses.
The variation of diffusion coefficient \( D \) with temperature is usually plotted with axes of \( \ln(D) \) and \( 1/T \). Diffusion in crystalline specimens results in a straight line fit for such a plot, indicating that \( D \) and \( T \) are related by the Arrhenius equation;

\[
D = D_0 \exp\left(-\frac{Q}{kT}\right) \quad \cdots 2.7
\]

Here \( D_0 \) depends on the geometrical factor \( \alpha \), the vibration frequency of diffusing atoms \( f \), and the diffusion jump distance \( d \), in the following way;

\[
D_0 = \alpha fd^2 \exp(\Delta S/K) \quad \cdots 2.8
\]

\( \Delta S \) and \( Q \) are the activation entropy and the activation energy of an individual jump.

Fig. 2.19 shows an Arrhenius plot of the measured diffusion coefficients in TM-M amorphous alloys, with the diffusion coefficient normalised by a factor;

\[
\frac{1}{a^2V} \quad \cdots 2.9
\]

\( V \) is the characteristic atomic vibration frequency and \( a \) is the characteristic atomic distance in the amorphous alloy. Further the temperature axis is scaled to \( T_g \). The resulting sets of data display Arrhenius behaviour, and a progressive change in diffusion mechanism with increasing size of the diffusing species.

Fig. 2.20 shows a similar plot for the more restricted data available for TM-TM amorphous alloys. The magnitude of the diffusion coefficients is similar to that in TM-M glasses, but some evidence of non-Arrhenius behaviour may be seen for boron diffusing in NiNb. Cantor and Cahn justify this observation by pointing out that the Arrhenius equation depends on all possible diffusion jumps being identical. For true random walk diffusion in a crystalline lattice
Fig. 2.20. Normalised Arrhenius plots for TM-TM glasses showing some non-Arrhenius trends.
the values of $\alpha$, $d$, $\Delta S$ and $Q$ will be identical from one jump to the next. In an amorphous alloy these parameters will vary from one jump to the next, so one cannot be certain that equation 2.7 is applicable. Actually it seems sensible to assume that if the amorphous structure were totally stable diffusional processes would follow Arrhenius behaviour, with the values of $\alpha$, $d$, $\Delta S$ and $Q$ being averages over the diffusional range of the experiment. Unfortunately it is possible that experiments revealing non-Arrhenius behaviour took place over such a time that the average values of the aforementioned parameters changed. The anomalous behaviour could then be explained in terms of structural relaxation. So a problem with measuring diffusion coefficients in metallic glasses is that, if the material is not "fully relaxed", the experiment itself may have a significant effect on the glassy structure. The fully relaxed state means the state in which only intrinsic defects are present in the structure.

As with crystalline metals it seems that metallic glasses allow both interstitial and substitutional types of diffusion mechanism. However the presence of more free volume in the glass lends an uncertainty to the energetics of each diffusional step. Results indicate that large atoms diffuse more easily in an amorphous structure than in the crystal, whilst small atoms find progress relatively more difficult. The non-Arrhenius observations for TM-TM glasses may result from structural relaxation; TM-M glasses do not display such behaviour because some metalloid atoms are located in "Bernal holes" and make the structure more rigid.
3 Inert Gas Bubbles in Metals

3.1 Introduction

In the introductory chapter of this thesis, many of the effects likely to occur in materials used for fusion applications were mentioned. Although ideally all tests on potential fusion reactor materials would be performed in situ, this usually proves impractical, because of financial and time constraints. Some of the most important effects can be studied through model situations. This thesis, for example, will employ inert gas ion irradiation facilities to; create displacement damage, cause the growth of inert gas bubbles, produce surface blisters and flakes, and reveal the effects of sputtering. This chapter is concerned with the details of these particular processes. The differences in performing this type of study on amorphous, as opposed to crystalline alloys, will be emphasised.
3.2 Displacement Damage in Metals

During the bombardment of metals with high energy particles, atoms in the target material are displaced. In crystalline metals the result is the formation of Frenkel defects (vacancy-interstitial pairs). For inert gas ions classical approximations can be used to describe the interactions. The maximum energy transferred to the stationary atom by the incident ion is given by:

$$E_m = \frac{4m_1 m_2 E_0}{(m_1 + m_2)^2}$$  \hspace{1cm} (3.1)

where $m_1$ and $m_2$ are the masses of incident and target particles. $E_0$ is the kinetic energy of the incident particle. For a Frenkel defect to be created, $E_m$ must exceed $E_d$, the atomic displacement energy. If the amount of energy transferred to the target atom is significantly more than $E_d$, it may subsequently be able to displace other atoms from their lattice sites. In such a situation a cascade of point defects would result from the initial collision or primary event. A diagram of a modelled displacement cascade is shown in fig.3.1. An estimate of the number of displacements caused by an incident atom can be gained from the expression:

$$N = \frac{E_0}{2E_d}$$  \hspace{1cm} (3.2)

$N$ can be a very large number, and as shown in fig.3.2 a cascade results in a core of vacancies surrounded by interstitials. Many of the defects created will annihilate each other; the number that do so increases with increasing temperature. It seems likely that around 99\% of the point defects created are lost through recombination.
**Fig. 3.1.** A projection of knock-on atom trajectories on a (001) plane in a 5keV displacement spike in Fe.

**Fig. 3.2.** The projected damage created in the (001) plane by the cascade in Fig. 3.1. Open squares are vacancies, filled circles are interstitials which outline the periphery of the damaged region.
Most of the computer codes, developed in the past to calculate damage and range profiles did not include the effects of crystallinity. If incident ions enter a crystal and are travelling parallel to a lattice plane, their penetration will be greater than if they were travelling at an angle to low index atomic planes. This effect is known as channelling and has been experimentally demonstrated by Verbeck and Eckstein ['74]. Their samples were polycrystalline molybdenum and the difference in ion penetration for each grain manifested itself as differences in blister size, density and shape. Similar conclusions have been drawn by Milaceke and Daniels ['68] from their respective experimental results.

For an amorphous alloy, channelling effects will be absent. In fact the computer codes so far developed may be more accurate for amorphous samples than for crystalline ones, where crystal orientation will have some effect on ion range.

The generation of true point defects cannot occur in an amorphous target. Indeed very little is known about the type of defects produced by irradiating amorphous alloys. The technique which yields the most useful data about this problem is positron annihilation. The following section is a review of results produced by positron annihilation studies, which are relevant to this thesis.
3.3 Positron Annihilation

As described in chapter 2 metallic glasses are less dense than their crystalline counterparts. They therefore contain more free volume. The sizes of free volume regions in metals can be studied with the aid of positron annihilation, because free volume is effectively a region of low electron density. If a region has a low electron density trapped positrons will have a longer lifetime than that of the average positron in the metal. The lifetime of positrons in the metal depends on the local density of electrons, so larger regions of free volume trap positrons for longer periods.
When positron annihilation has been used to study unirradiated amorphous alloys, the following qualitative conclusions have been drawn [Gopinathan '84]:

(i) Traps are generally smaller than single vacancies detected in crystalline metals. Some idea of the size of the largest traps, and the fraction of free volume they take up, can be found in section 2.2.

(ii) The trap concentration is higher in metallic glasses containing a metalloid component, than those consisting of transition metal elements.

(iii) The dense random packing model of amorphous alloy structures (see section 2.2), suggests that metalloid atoms lie in what would be the largest free volume regions of a glass. Positron annihilation studies support the random packing models through the hole sizes they predict, and the location of metalloid atoms they imply.
(iv) Anomalously, trap size increases with increasing temperature in metalloid-containing glasses, but decreases in glasses solely containing transition metals. It has been suggested that this result indicates that atoms rearrange themselves more easily in transition metal glasses.

(v) Reversible property changes, brought about by structural relaxation, are due to local atomic movement; the average trap density remains unchanged.

An important result from the point of view of irradiation damage is that:

(vi) Trap sizes increase during neutron or electron bombardment at low temperatures (near 70K). This increase in trap size is lost as the specimens are annealed to 300K. The loss occurs smoothly with increasing temperature, suggesting that a continuous range of defect sizes is produced. This is to be expected in a material where the atoms are randomly distributed about a mean separation [Audouard et al '83].

For crystalline alloys a small percentage of vacancy-sized defects are expected to remain after such an irradiation and heat treatment. The conclusion to be drawn from this result is that radiation induced defects which occur at room temperature in metallic glasses are unlikely to be stable. Support for this belief has also been provided by the theoretical considerations of Bennett et al ['79], who modelled atomic size holes in a random array of hard spheres, and found them to be unstable.
3.4 Bubble Nucleation

3.4.1 Diffusion and Trapping of Inert Gas Atoms in Metals

This section describes some of the effects thought to occur during the early stages of implantation, before observable changes in the microstructure have taken place. Fig.3.3 shows the depth distributions of damage and implanted ions expected to occur during 100keV helium ion implantations of amorphous CuZr. As soon as ions have lost the kinetic energy that took them into the specimen they may be diffusively mobile or they may be trapped. In the case of inert gas atoms trapping processes lead to the formation of bubble nuclei. Rimmer and Cottrell [57] and Melius et al [80] have shown theoretically, that helium and neon atoms reside interstitially in copper and nickel respectively, when lattice defects are absent. For the larger inert gas atoms i.e. argon, krypton and xenon however, a substitutional situation is energetically more favourable (see table 3.1). The mobility of interstitial inert gas atoms is very high, so when vacancies are present, helium and neon will quickly take up substitutional sites. Johnson et al have calculated that even helium will favour substitutional sites to a significant extent. Their theoretical values are given in table 3.2 [Johnson et al 71]

Some idea of the high mobility of inert gas atoms in
Fig. 3.3. The damage and ion concentration profiles that result from 100keV He\(^+\) implantations of amorphous CuZr. The calculation used the EDEP code.
### TABLE 3.1.

After Rimmer and Cottrell '57.

<table>
<thead>
<tr>
<th>Type of Solution</th>
<th>Energy terms</th>
<th>He</th>
<th>Ne</th>
<th>A (a)</th>
<th>A (b)</th>
<th>Kr (c)</th>
<th>Kr (d)</th>
<th>Xe (e)</th>
<th>Xe (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial</td>
<td>Strain</td>
<td>1.7</td>
<td>2.4</td>
<td>10.6</td>
<td>7.7</td>
<td>14.9</td>
<td>10.8</td>
<td>24.5</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>Electronic</td>
<td>0.6</td>
<td>1.2</td>
<td>3.0</td>
<td>2.3</td>
<td>4.6</td>
<td>3.0</td>
<td>6.5</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>$E_s$</td>
<td>2.5</td>
<td>4.6</td>
<td>13.6</td>
<td>10.0</td>
<td>19.5</td>
<td>13.8</td>
<td>31.0</td>
<td>22.4</td>
</tr>
<tr>
<td>Substitutional</td>
<td>Strain</td>
<td>0</td>
<td>0.3</td>
<td>2.2</td>
<td>1.7</td>
<td>3.8</td>
<td>2.7</td>
<td>7.8</td>
<td>5.7</td>
</tr>
<tr>
<td>(problem 2)</td>
<td>Electronic</td>
<td>0</td>
<td>0.1</td>
<td>0.7</td>
<td>0.5</td>
<td>1.4</td>
<td>0.8</td>
<td>2.4</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>$E_s$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Substitutional</td>
<td>$E_{S_1}$</td>
<td>1.0</td>
<td>1.4</td>
<td>3.9</td>
<td>3.2</td>
<td>6.2</td>
<td>4.5</td>
<td>11.2</td>
<td>8.2</td>
</tr>
<tr>
<td>(problem 1)</td>
<td>$E_{S_1}$ ( = $E_{S_1} - E_I$)</td>
<td>5.5</td>
<td>5.9</td>
<td>8.4</td>
<td>7.7</td>
<td>10.7</td>
<td>9.0</td>
<td>15.7</td>
<td>12.7</td>
</tr>
</tbody>
</table>
**TABLE 3.2**  

Substitutional detrapping energies in fcc and bcc metals. Values in parentheses are the relative energies of a helium atom in a vacancy and in an interstitial position.

<table>
<thead>
<tr>
<th></th>
<th>Formation Energy, in eV, of a He Atom in a Vacancy</th>
<th>Formation Energy, in eV, of a HeInterstitial</th>
<th>Substitutional Detrapping (Popout) Energy, in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.15</td>
<td>2.03</td>
<td>(1.88)</td>
</tr>
<tr>
<td>Ni</td>
<td>1.36</td>
<td>4.52</td>
<td>(3.16)</td>
</tr>
<tr>
<td>Pd</td>
<td>0.52</td>
<td>3.68</td>
<td>(3.16)</td>
</tr>
<tr>
<td>Ag</td>
<td>0.0</td>
<td>1.53</td>
<td>(1.53)</td>
</tr>
<tr>
<td>Fe</td>
<td>1.61</td>
<td>5.36</td>
<td>3.98 (3.75)</td>
</tr>
<tr>
<td>Mo</td>
<td>1.04</td>
<td>4.91</td>
<td>4.19 (3.87)</td>
</tr>
<tr>
<td>W</td>
<td>1.05</td>
<td>5.47</td>
<td>4.75 (4.42)</td>
</tr>
<tr>
<td>V</td>
<td>1.65</td>
<td>4.61</td>
<td>3.20 (2.96)</td>
</tr>
<tr>
<td>Ta</td>
<td>0.93</td>
<td>4.23</td>
<td>3.44 (3.30)</td>
</tr>
</tbody>
</table>
interstitial sites can be obtained by comparing their activation energy for migration with that of vacancies in the target material. Two examples are given in the table below.

Table 3.3.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Target Metal</th>
<th>$\Delta H$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial He</td>
<td>Tungsten</td>
<td>0.29</td>
<td>Casper '74</td>
</tr>
<tr>
<td>Vacancy</td>
<td></td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Interstitial Ar</td>
<td>Molybdenum</td>
<td>0.33</td>
<td>Van Veen '82</td>
</tr>
<tr>
<td>Vacancy</td>
<td></td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

Work by Kornelson ['72] on the thermally induced de-trapping of helium in tungsten has shown that low energy implanted helium ($E_0<500$eV) is not trapped. This is because the implant creates very little displacement damage. If however, the target is pre-damaged by a heavier ion then most of the helium is trapped.

Melius et al ['80] have calculated the formation and migration energies for inert gas atom-vacancy complexes in fcc nickel, for He, Ne, Ar, Kr and Xe. These complexes will be represented in the form $I_mV_n$ in this thesis, where the subscripts $m$ and $n$ indicate the number of each species present. Melius and Wilson suggested that all substitutional gas atoms i.e. the $I_1V_1$ species, are relatively mobile. This mobility is unlikely to be enhanced by trapped self-interstitials (i.e. to produce $I_mV_{n+1}$ complexes); as although a mechanism for such complexes to migrate would require little energy for diffusion to occur, these complexes are unstable (see table 3.4). However, the $I_1V_2$ complexes do show enhanced
mobility and reasonable stability. The calculated results are presented in the table below.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Migration</th>
<th>Break Up (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeV</td>
<td>3.26</td>
<td>3.36</td>
</tr>
<tr>
<td>NeV</td>
<td>5.13</td>
<td>5.33</td>
</tr>
<tr>
<td>ArV</td>
<td>6.98</td>
<td>7.42</td>
</tr>
<tr>
<td>KrV</td>
<td>8.06</td>
<td>7.83</td>
</tr>
<tr>
<td>XeV</td>
<td>8.52</td>
<td>8.01</td>
</tr>
<tr>
<td>HeVi</td>
<td>0.88</td>
<td>0.69</td>
</tr>
<tr>
<td>NeVi</td>
<td>0.47</td>
<td>0.37</td>
</tr>
<tr>
<td>ArVi</td>
<td>1.69</td>
<td>0.81</td>
</tr>
<tr>
<td>KrVi</td>
<td>2.32</td>
<td>1.04</td>
</tr>
<tr>
<td>XeVi</td>
<td>2.76</td>
<td>1.30</td>
</tr>
<tr>
<td>HeV₂</td>
<td>1.35</td>
<td>1.87</td>
</tr>
<tr>
<td>NeV₂</td>
<td>1.53</td>
<td>1.96</td>
</tr>
<tr>
<td>ArV₂</td>
<td>1.68</td>
<td>2.37</td>
</tr>
<tr>
<td>KrV₂</td>
<td>1.84</td>
<td>2.73</td>
</tr>
<tr>
<td>XeV₂</td>
<td>2.14</td>
<td>3.44</td>
</tr>
</tbody>
</table>

If we regard the growth of $I_mV_n$ complexes, to a size when stochastic fluctuations in the flux of defects are unlikely to destroy them, as "bubble nucleation"; the mobility of $IV_2$ complexes may be the rate controlling factor for nucleation.

Self-interstitials in the target metal will displace helium and neon from $I_mV_n$ complexes. However, ejected gas atoms will rapidly diffuse through the structure to be retrapped. The
stability of $I_{mV_n}$ complexes depends on the in and outgoing fluxes of vacancies, interstitials and other $I_{mV_n}$ complexes. The relative magnitude of these fluxes, and hence the stability of an $I_{mV_n}$ cluster against annihilation, is affected by many material and implantation parameters. Besides stochastic effects, the following factors are influential:

(i) The pressure of gas within the complex. This can cause a strain field to exist around the complex. According to the theory of strain field interaction with lattice point defects, both vacancies and interstitials are attracted by strain fields. However, a short range repulsion of interstitials exists because the bubbles are overpressurised. A similar, but lesser attraction exists between $I_{mV_n}$ complexes and the $I_{1V_1}$ species.

(ii) The preferential trapping of self-interstitials at grain-boundaries and precipitates. A depletion of self-interstitials ensures a surplus of vacancies around such microstructural features, and so favours a net flux of vacancies and the $I_{1V_1}$ species to larger $I_{mV_n}$ complexes.

(iii) Enhanced diffusion of inert gas atoms, aided by the presence of grain boundaries.

Both points (ii) and (iii) lead to distinct fluctuations in the local growth rate of $I_{mV_n}$ complexes. They tend to locally increase the likelihood of $I_{mV_n}$ complexes reaching a size which will make them effectively immune to
stochastic annihilation. According to these considerations a higher density of bubbles should occur at grain boundaries and precipitates than in the defect free metal. Observations confirming the validity of this conclusion have been made by Lane and Goodhew ['84].

(iv) The magnitude of binding energies for inert gas atoms and vacancies. Clearly the higher the binding energy for each successive element of the ImVN cluster, the more energetically stable that cluster is. Binding energies for helium atoms and vacancies to He_mVN complexes in copper were calculated by Wilson [See Reed '77]; the results are displayed in table 3.5. Helium atoms are lightly bound to complexes, and their binding energy falls with increasing 'm'. Conversely vacancy binding energy increases with increasing 'm'. The most stable configuration will occur when the highest simultaneous values of He and vacancy binding energies exist. Table 3.5 indicates that this occurs for 'n=m'. Reed comments on the scale of these binding energies pointing out that such complexes would be energetically stable up to about 0.4 of the melting point (T_m). Defects with the ImVN, m-n format form the most likely route to bubble nucleation.
TABLE 3.5.

Binding energies of the $n$th helium atom and the $m$th vacancy in a He$_n$V$_m$ cluster in copper (see Reed '77).

<table>
<thead>
<tr>
<th>$n$</th>
<th>$m$</th>
<th>$E_{U_{11}}$</th>
<th>$E_{V_{11}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.08</td>
<td>0.18</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>0.08</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0.58</td>
<td>0.71</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>1.84</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Note: The values in parentheses are the binding energies in electron volts (eV).
3.4.2 Modelling Bubble Nucleation

As described in section 3.4.1 bubble nucleation is considered to be the chance accumulation of inert gas atoms and vacancies, so that a \( \text{I}_m\text{V}_n \) complex is created. This complex is said to form a stable nucleus, when the energy needed for an atom to leave the cluster prevents the cluster losing atoms faster than they arrive. Greenwood et al ['59] suggest that a cluster of 3 to 6 inert gas atoms with a few vacancies would have a binding energy of \(-3\text{eV}\). As a result such a cluster would have a lifetime against thermally aided atom loss of \(~100\text{ secs}\). It is worth noticing that a binding energy of \(2\text{eV}\) would give a lifetime of \(~10^{-2}\text{s}\); so the stability of a cluster is extremely sensitive to the estimate of binding energy.

Greenwood et al also reviewed experimental reports and suggested that the diffusion coefficient of inert gas atoms in polycrystalline uranium is \(~10^{-17}\text{m}^2\text{s}^{-1}\) at 900K. In their view irradiation is unlikely to affect the gas diffusion coefficient above 900K; although below this temperature, some enhanced diffusion might be expected.

To develop a model of bubble nucleation a great number of factors must be taken into account. The problem is so involved that major assumptions must be made. Greenwood et al made the following assumptions:

(i) Gas atom diffusion is aided by vacancies, and a stable
nucleus is formed by $I_2V$, i.e. a gas atom plus an $I_1V_1$ complex that migrates to it.

(ii) The steady state diffusion equation can be applied i.e.

$$D \frac{\partial^2 c}{\partial r^2} = -G \quad \text{.....3.3}$$

with $D$ the gas diffusion coefficient, $c$ the atomic concentration of gas and $G$ the rate of gas atom production per atomic site per second.

(iii) For bubble nuclei of radius $r_0$ and an average separation of $2r_1$, the boundary conditions for the diffusion equation are;

$C=0$ at $r=r_0$ and $dc/dr=0$ when $r=r_1$.

(iv) $r_1 \gg r_0$

(v) The number of nuclei increase until a newly created gas atom is more likely to meet a nucleus than another single gas atom.

They concluded that the homogeneous nucleation separation, $2r_1$, will be determined by;

$$r_1^6 = 3D r_0^2 a^2 / 2GZ \quad \text{.....3.4}$$

where $D$ is the gas diffusion coefficient, $r_0$ is the bubble radius, $a$ is the atomic size of the metal atoms, $G$ is the gas arrival rate in ions per atom and $Z$ is a geometrical factor taken to equal 4.

In their treatment Greenwood et al expanded this result to include the presence of dislocations in the metal matrix. Such factors will not be enlarged upon here, as they should not affect bubble nucleation in an amorphous alloy. At a later stage of
this thesis, equation 3.4 will be applied to experimental observations, so that an estimate can be made of the gas diffusion coefficient in an amorphous alloy.

More complex nucleation analyses have been described by Russell ['78], Singh and Foreman ['75], and Wiedersich et al ['74]. The considerations made are detailed, but interpretation of the equations for amorphous alloys is difficult. As a result of the lack of a structural model for amorphous alloys, experimentally verifiable theories require considerable simplifications.

3.5 Bubble Growth

Four mechanisms of bubble growth are described in this section. They have been used to explain growth under a wide range of experimental conditions, but each is favoured by certain conditions. The specimen temperature, and hence the equilibrium density of point defects, is a particularly important factor. The brief table below serves to show which mechanism might be expected to dominate bubble growth, under different temperature regimes.

Table 3.6.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-Vacancy Accumulation</td>
<td>$T &gt; 0.5T_m$</td>
</tr>
<tr>
<td>Migration and Coalescence</td>
<td>$T &gt; 0.5T_m$</td>
</tr>
<tr>
<td>Athermal Processes</td>
<td>$T &lt; 0.3T_m$</td>
</tr>
<tr>
<td>Bubble Ripening</td>
<td>All $T$ (cascade aided)</td>
</tr>
</tbody>
</table>
In addition, bubble growth is favoured by continued irradiation, through the energy it deposits into the target. This increases the mobility and concentration of point defects by increasing the target temperature. It also increases the concentration of point defects beyond the thermal equilibrium value through atomic displacements. As a result radiation damage increases the mobility of impurities which prefer substitutional sites within the material. Radiation damage thus leads to the possibility of radiation enhanced diffusion (RED). Of the mechanisms described above radiation is thought to aid bubble ripening in particular because cascades would lead to an increased probability of inert gas atoms re-entering the metal matrix.

Each of the processes mentioned above will be discussed in detail here, but for more quantitative evaluations of which temperature regimes favour each mechanism, the reader should refer to Goodhew ['84].

3.5.1 Gas-Vacancy Accumulation

One highly simplified way of considering bubble growth is to assume that once a certain density of bubble nuclei has formed, nucleation ceases. Thereafter gas arriving in the sample diffuses to one of those nuclei, so that the contained gas pressure increases. Growth then depends on a means of relieving the increased pressure.
The easiest conditions under which pressure is relieved occur at elevated temperatures, \( T > 0.5T_m \), when both the equilibrium density, and the mobility of vacancies are high. This section will deal with a model of bubble growth adopted early in the course of inert gas bubble studies. The model is now known to apply only when the specimen temperature is above \( 0.5T_m \). It follows that bubbles will receive a large number of vacancies, and hence increase their volume sufficiently rapidly for their internal pressure to be approximately given by equation 3.28.

The growth of inert gas bubbles in solids as a result of constant gas generation has been analysed by several workers including Speight ['68] and Cornell ['69] and Markworth ['69]. The treatment pursued by Markworth involved the following assumptions:

(i) The gas in the bubbles behaves ideally.
(ii) Gas is restrained purely by surface tension.
(iii) Surface tension, \( \gamma \), is independent of direction.
(iv) Homogeneous bubble nucleation.
(v) A solid free of sinks for gas atoms other than bubbles.

The use of the ideal gas law is now accepted as an erroneous assumption, particularly for small bubbles as these are thought to contain gas under high pressures (see equation 3.30). Also, assuming surface tension to be the only restraint for gas pressure implicitly suggests that vacancies are abundant and mobile within the matrix. Under many conditions this will not be
Combining (i) and (ii) above, allows the derivation of the following simple relationship between bubble radius \( r_b \) and the number of contained gas atoms \( N \);

\[
8\pi\gamma r_b^2/3 = Nk_B T \tag{3.5}
\]

The flow of gas atoms towards bubbles was estimated using assumptions (iv) and (v). With the equilibrium concentration of gas in the solid being effectively zero, the rate of gas atom arrival at each bubble can be expressed as;

\[
\frac{dN}{dt} = 4\pi D r_b C_g \tag{3.6}
\]

\( D \) is the diffusion coefficient for gas atoms in the solid and \( C_g \) is the gas concentration in the solid far from bubbles. Equations 3.5 and 3.6 give;

\[
\frac{dr_b}{dt} = 3k_B T D g C_g /4\gamma \tag{3.7}
\]

Assuming finally that the following expression for the total number of gas atoms is given by;

\[
Q_t = C_g + nN \tag{3.8}
\]

where \( n \) is the number of bubbles per unit volume and \( Q \) is the gas arrival rate. Markworth replaced \( C_g \) and \( N \) using equations 3.7 and 3.5 to give;

\[
Q_t = (4\gamma/3k_B T g D G) (dr_b/dt) + (8\pi\gamma n/3k_B T) r_b^2 \tag{3.9}
\]

His analytical solution of this equation yielded the following asymptotic expressions for \( r_b \) and \( C_g \), as functions of time, \( t \);

\[
r_b \sim (3kTQ_t/8\pi\gamma n)^{1/2} \tag{3.10}
\]

\[
C_g \sim (\gamma Q/b\pi nk TD g^2 t)^{1/2} \tag{3.11}
\]

The assumptions made in this treatment are probably more
applicable to amorphous alloys than crystalline ones, because fewer inhomogeneities exist in the former. Several assumptions discussed here will be considered again in chapter 7.

3.5.2 Migration and Coalescence

(a) Migration

A well established mechanism by which bubbles grow involves their migration, the meeting of two bubbles followed by their coalescence to form one larger bubble. Theories describing this mode of growth have been reviewed and developed by Goodhew and Tyler ['81], Nichols ['69] and Willertz and Shewmon ['70]. The movement of a bubble through a solid matrix requires the net removal of atoms from one side and the net addition of atoms at the opposite side. This can be assisted by an external influence, such as a thermal gradient or an applied stress, in which case the bubble velocity is described by the Nernst-Einstein equation;

\[ V = \frac{D_b F}{kT} \quad \text{(3.12)} \]

where \( D_b \) is the diffusion coefficient of the bubble and \( F \) is the driving force for migration. In the absence of a driving force, bubble motion can be considered through a probabilistic approach similar to that used to describe Brownian motion.

Equations for bubble diffusion coefficients can be derived by considering the geometrical aspects of transferring atoms from one position to another. The three dimensional random walk
equation for diffusion gives simply;

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

where $\Gamma_b$ is the jump frequency for the bubble and $\lambda_b$ is the average jump distance.

We can now consider the three mechanisms by which atoms may be effectively transferred from one side of the bubble to the other;

(i) Surface Diffusion

The number of atoms at the bubble surface participating per unit jump of pore is given by:

$$4\pi r_b^2 / \lambda^2$$

where $\lambda$ is the average jump distance for the diffusing (rate-controlling) species. The jump frequency for the bubble can be related to that of the diffusing species by the number of surface atoms participating per unit bubble jump ($4\pi r_b^2 / \lambda^2$);

$$\Gamma_b = \Gamma_s (4\pi r_b^2 / \lambda^2)$$

$\Gamma_s$ is the jump frequency of the surface diffusing species. For the bubble to move through a given distance, $4\pi r_b^3 / \Omega$ atoms must be transported in the opposite direction to the bubble motion ($\lambda^3 = \Omega$ is the average atomic volume). This leads to the following relationship between atom jump distance and bubble jump distance;

$$\lambda_b = \frac{3}{4} \Omega / \pi r_b^3$$

The atomic diffusion coefficient in two dimensions can be obtained from;

$$D_s = \frac{1}{4} \Gamma_s \lambda^2$$
so that combining equations 3.16 and 3.17 we obtain;

\[ D_b(s) = \frac{3D_s \lambda \Omega}{2 \pi r_b^4} \] ......3.18

(ii) Volume Diffusion

This process of bubble motion involves atoms leaving one side of the bubble and atoms joining the opposite side. Using an analogous treatment to that applied to surface diffusion we can obtain;

\[ D_b(v) = \frac{3D_v \Omega}{4 \pi r_b^3} \] ......3.19

where \( D_v \) is the self diffusion coefficient for atoms in the solid.

(iii) Vapour Transport

For this process the treatment is identical to that used for volume diffusion, except that differences, between the density of atoms in the bubble and those in the metal, must be taken into account. The equation derived is as follows;

\[ D_b(g) = \frac{3Dg \Omega^2 Pq}{4 \pi r_b^3 kT} \] ......3.20

where \( P \) is the vapour pressure of the solid and \( q \) is a measure of the extent to which the gas deviates from ideality.

It should be noted that the equations derived above assume spherical bubbles are involved. The conversions required for them to apply to cubic bubbles (these are usually needed for crystalline solids, as suggested in section 3.7) are straightforward, and have been demonstrated by Goodhew and Tyler ['81]. The equations have been presented in the above form, because bubbles in the isotropic matrix of an amorphous alloy
should be essentially spherical. If faceted bubbles are to be considered, some account must be taken of ledge nucleation energies of each facet. Goodhew and Tyler ['81] have shown that the nucleation of a ledge on a facet that is losing atoms is likely to be the rate controlling step for the migration of faceted bubbles. If the surface energy per unit length of a monatomic ledge is $\xi$, it can be deduced [Tyler and Goodhew '78] that the bubble diffusion coefficient for a cubic bubble migrating in surface diffusion but limited by ledge nucleation is given by;

$$D_b(f) = (\pi D_s a/6\lambda) \exp(-\pi a c/2kT) \quad \cdots 3.21$$

where $a$ is the side length of the bubble.

In section 3.7 the presence of impurities at the surface of a bubble (e.g. oxygen or nitrogen in surface layers) is mentioned as a factor affecting the kinetics leading to an observed bubble shape. If such layers affect local atomic mobility to the extent that they decide the shape of a bubble, then it is probable that they will affect bubble migration. The presence of a contamination stabilised layer at bubble surfaces may well result in reduced bubble mobility. As an example we can consider the case of an ionic oxide at the bubble-metal interface. Atoms on the oxide surface would be less mobile than atoms on the surface of the pure metal.

Aitken et al have demonstrated that for small bubbles ($r_b < 1.5\text{nm}$) in the temperature range 950-1250°C the rate controlling process for bubble migration is surface diffusion. [Aitken et al '73]. In fact it seems likely that surface
diffusion dominates mobility at all temperatures, for bubbles large enough to be observed in the TEM (i.e. \( r_b > 0.5 \text{nm} \)). Some attempt to map which growth mechanisms dominate as temperature and bubble size are varied is currently being undertaken by Goodhew et al [87]. Their results indicate that under most circumstances where bubble growth is possible the mechanism is coalescence, with surface diffusion providing the means for migration.

(b) Coalescence

In the previous section bubble migration was discussed in some detail, with no mention of coalescence. This was because coalescence is unlikely to be the rate controlling step for this mechanism. Experimental evidence for the ease with which coalescence occurs was provided by Barnes and Mazey [63]. Their observations revealed coalescence occurring rapidly Lidiard and Nelson [69] have shown theoretically that a short range attraction exists between bubbles, and that coalescence is probably assured once bubbles come within one or two bubble radii of each other.

Initially when two bubbles collide, bubble volume is conserved in the coalescence. Let us assume the new bubble radius is given by;

\[
r_3^3 = r_1^3 + r_2^3
\]

Several interesting points result from this relation:

(i) The surface energy \( (G_s) \) is reduced by a coalescence,
because the final surface area is less than that of the two colliding bubbles; i.e. $\Delta G_s$ is negative.

(ii) Simultaneously the strain energy ($G_{st}$) of the matrix surrounding the bubble is increased i.e. $\Delta G_{st}$ is positive.

(iii) The total change in free energy is:

$$\Delta G = \Delta G_s + \Delta G_{st} \quad \text{...3.23}$$

if we assume that the gas behaves ideally, the change in gas free energy is zero. Then, since $\Delta G_s$ is larger than $\Delta G_{st}$, for bubbles of radius greater than 0.1 nm, coalescence is thermodynamically favoured.

Following coalescence some change in bubble volume is needed, if the contained gas is to be in equilibrium with the surrounding solid. In the case of bubbles whose internal pressure is relatively low (for the upper limit see the following section on athermal bubble growth) this relaxation requires vacancies to be present and mobile in the solid. If this is the case (e.g. at $T > 0.5T_m$ in crystalline metals), overpressurised bubbles can grow and underpressurised bubbles must shrink. If the internal pressure is sufficiently high a rapid means of growth may be preferred. This involves athermal processes and will be discussed in the next section. Using the ideal gas law we can write:

$$P_3 V_3 = P_1 V_1 + P_2 V_2 \quad \text{...3.24}$$

and hence for equilibrium bubbles, where the internal gas pressure is given by equation 3.30;

$$r_3^2 = r_1^2 + r_2^2 \quad \text{...3.25}$$
Problems which are scientifically similar to those encountered when considering bubble coalescence have been tackled in connection with the coagulation of colloids. A finite difference equation describing coalescence has been proposed by Chandrasekhar [43]. The number of coalescences between i and j bubbles in the short time interval $\Delta t$ is given by:

$$\Delta F_{ij} = 4\pi D_{ij} R_{ij} F_i F_j \{1 + [R_{ij}/(\pi D_{ij} t)^{0.5}]\} \Delta t \quad \ldots \quad 3.26$$

$F_i$ and $F_j$ are the number of i and j bubbles per unit volume, $D_{ij}$ is the sum of the diffusion coefficients of i and j bubbles. This type of approach has been employed by several workers in the field of inert gas bubble research, notably Gruber [67] and Mikhlin and Chkuaseli [75].

Gruber used this random migration and coalescence equation with an estimated bubble diffusion coefficient, to model bubble evolution. The diffusion coefficient was obtained from atomic surface diffusion considerations. His analysis began with bubbles containing only one gas atom, and he assumed that the gas behaved ideally. Bubbles were also taken to be in equilibrium with the surface tension forces of the solid. Goodhew and Tyler [81] extended this treatment to deal with faceted bubbles. The approach adopted by Mikhlin and Chkuaesi was similar although their calculations permitted non-ideal gas behaviour. This is more appropriate for small bubbles, where the internal pressure may be high. Their results indicated that bubble migration in $\text{UO}_2$ is likely to be the result of surface diffusion, but that in alumina volume diffusion is preferred. These conclusions demonstrate the usefulness of this type of approach. However a rationale for the growth mechanism must be developed.
Under conditions where athermal bubble growth is necessary (i.e. when the mobility of vacancies is negligible), the magnitude of the pressure contained in the bubble is less easily evaluated. There have been several reports of bubbles ejecting interstitials into the surrounding solid. The point defects created associate, so that a dislocation loop is formed [Evans et al '81a and '83, Greenwood et al '59]. The energetics of dislocation loop production suggest that the upper limit on internal gas pressure is given by;
\[
p = \mu b \ln\left(\frac{r_b}{b}\right) / 2\pi r (1 - \nu) + 2\gamma / r \tag{3.27}
\]
where \( b \) is the Burgers vector of the dislocation loop formed, \( \mu \) is the shear modulus of the material and \( \nu \) is Poisson's ratio. Evans and Mazey have used the few existing evaluations of internal gas pressure to show that this expression holds quite well for small bubbles at ambient temperature [Evans and Mazey '86]. The pressures involved for bubbles under such conditions are extremely high; probably in the region of several GPa. In fact this high pressure can cause the inert gas to solidify at room temperature, allowing the atom spacing to be measured from electron diffraction patterns [Cox et al '86]. The presence of high bubble pressures is also supported by ultra-violet spectroscopy [Donnelly et al '73] and electron energy loss spectroscopy [Rife et al '81, Jager et al '83, Donnelly '85]. Clearly for bubble growth the pressure should exceed the value given by equation 3.27. This value is high, so only the smallest bubbles with \( r_b < 2 \text{nm} \) are likely to fulfill this criterion.
The growth of bubbles in amorphous alloys is not well understood, because the energy required to create either 'vacancy type' or 'interstial type' defects is not easily evaluated. However, according to Evans and Mazey ['86], the pressure in small bubbles can be approximated by the empirical relation;

$$p = \mu/(16\pm4)$$

Amorphous metals have shear moduli of a similar order of magnitude to crystalline metals, so the bubble pressure is not expected to be significantly different at a particular value of \( r_b \) for the two types of material.

### 3.5.4 Bubble Ripening

This mechanism of bubble growth involves gas from small bubbles going into solution, and the acceptance of this gas by larger bubbles. Although inert gas atoms are virtually insoluble in metals [Rimmer and Cottrell '57], we have already seen that the pressures within bubbles can be very high. As a result, there is a finite probability that some gas atoms will penetrate the metal around the bubble. The gas concentration near a bubble is given by the following equation, according to Rimmer and Cottrell;

$$\rho = p . \exp(\Delta S/k) \exp(-\Delta H/kT)$$

where \( p \) is the pressure within the bubble, \( \Delta S \) the internal entropy change in the lattice due to the presence of gas atoms and \( \Delta H \) is the heat of solution. If we assume the pressure within the bubble to be opposed by the surface tension of the metal.
(i.e. an equilibrium situation exists between the internal gas pressure and the surface tension), we can write:

\[ p = \frac{2\gamma}{r} \quad \ldots 3.30 \]

where \( r \) is the bubble radius and \( \gamma \) is the surface energy. Using this relationship and combining it with equation 3.29, we find that the highest gas concentration will exist around the smallest bubbles. A concentration gradient will effectively exist between small and large bubbles. This provides an explanation for the ripening process. The process is energetically favourable because it results in a reduction of gas pressure within bubbles, i.e. the overall free energy associated with the gas is reduced.

Barnes and Nelson ['65] compared the resolution growth process with bubble migration and coalescence in copper at 1200K, without continued irradiation. They concluded that resolution was not going to make a significant contribution to growth under these conditions.

Greenwood et al ['59] developed an equation for growth by bubble ripening through grain boundary aided gas diffusion. The gas concentration bound to grain boundaries was expressed in a similar way to that around bubbles and the two equations used to derive the relationship;

\[ r_2^3 - r_1^3 = A \frac{D \text{wft}}{2f\ln(L/R)} \exp \left\{ \frac{(H - U_b)/kT}{g} \right\} \ldots .3.31 \]

According to Markworth ['73], bubble ripening produces a characteristic distribution of bubble sizes. His theoretical work showed that the shape of the bubble size distribution remains the same, whilst growth takes place, i.e. the mean bubble size increases.
One factor making resolution an important means of bubble growth is the occurrence of high energy cascades. This has been studied comprehensively in relation to the fission reactor fuel, UO$_2$. Under reactor conditions the fission cascades each introduce ~100MeV of energy into the material. If this occurs sufficiently close to a bubble, gas may be released to migrate to other bubbles [Kitajima '84, Nelson '69].

It seems unlikely that the implantation energies employed during the course of this project (5-100keV) will cause significant gas resolution to occur, even though the bubble growth discussed took place while gas was entering the specimen.

3.6 Bubble Populations

It is almost inevitable that the study of inert gas bubbles will require the consideration of a range of bubble sizes. A combination of several phenomena leads to a distribution of bubble sizes forming within the target.

The major factors which contribute to the existence of a bubble distribution are:

(i) During implantation the rate at which gas atoms arrive in the specimen varies with depth. It has been suggested that this variation is approximately
Gaussian in shape and centred on the calculated mean projected range, $R_p$, (see fig. 3.3). Recalling equation 3.4 after Greenwood et al [59], this means that the density of bubble nuclei should vary similarly with depth. Also, equation 3.24 indicates that if bubbles can migrate, coalescences will occur most frequently in regions with the highest bubble density. Considering these factors alone we must conclude that the largest bubbles will occur near $R_p$, with smaller bubbles forming at lesser and greater depths.

(ii) If the equilibrium concentration of vacancies within the metal is low, the fact that most of the damage caused by the implantation occurs closer to the surface than $R_p$ (see fig. 3.3) may lead to slightly larger bubbles forming near the maximum in the damage distribution. The available vacancies will be more numerous in this region.

(iii) Athermal bubble growth is most likely to occur in the region where bubbles are most overpressurised. It may therefore result in more bubble growth beyond the maximum in the damage distribution, i.e. near or beyond $R_p$, where fewest vacancies are produced during implantation. This results from the type of damage distribution shown in fig. 3.3.

(iv) Bubble nucleation is expected to occur preferentially near grain boundaries and dislocations, as described in section 3.4.1. Near grain boundaries the increased nucleation density will lead to increased rates of coalescence.

(v) Recent attempts at studying bubble growth as a function of depth by cross-sectional specimen preparation, have shown that the specimen surface is a good source of vacancies.
Bubbles that are overpressurised accept vacancies until they attain equilibrium. As a result the bubbles nearest the surface are initially the largest in the size distribution. Once these bubbles equilibrate, vacancies pass on to those next nearest the surface. So the influence of the surface on bubble growth moves progressively through the bubble layer. This process is shown in fig.3.4 [Marachov et al '87].

During the early stages of bubble growth, the width of the bubble size distribution may be small. If this is the case the distribution is roughly Gaussian in shape (see fig.3.5). If the bubble size distribution can be approximated by a Gaussian, a mean size and the standard deviation from that mean can be used to represent it. However, in many cases the distribution is clearly not Gaussian. Fig.3.6 shows a distribution heavily skewed so that a long tail exists towards larger bubble radii. This particular example shows the effect of high temperature annealing for a long period of time. The skewness is probably compounded by the resolution limit of the TEM, which cannot reveal bubbles smaller than ~1nm in diameter. The mean bubble size does not represent the entire distribution in this case, because a large influence on the mean comes from a small number of very large bubbles. A better description of the distribution may be given by the modal value, particularly if migration and coalescence is being considered as the mechanism dominating bubble growth. It should also be noted that the coalescence rate depends on the speed with which bubbles migrate. This falls dramatically with increasing bubble size (see equations 3.18, 3.19 and 3.20). As a result the most common or
Fig. 3.4. Helium bubbles growing in Ni as a result of vacancy collection from the specimen surface. Samples were annealed at 750 K for: a) 6, b) 12, c) 20 and d) 100 hours.
Fig. 3.5. An example of a near-Gaussian distribution of bubble sizes.

Fig. 3.6. An example of a non-Gaussian distribution of bubble sizes.
modal bubble size (which is generally less than the mean size) is the best parameter to represent the population.

3.7 The Shape of Inert Gas Bubbles

As described in section 3.2 ion implantation causes displacement damage. In the absence of mobile inert gas atoms displacement cascades in crystalline metals collapse to form dislocation loops. It was assumed that when inert gas atoms were present, they would migrate to vacancies in the cascade, so that collapse produced a spherical bubble nucleus. The spherical shape would then be stabilised by the internal pressure of gas. Experimental observations have shown however, that two dimensional platelets of inert gas form in some cases [Evans et al '81a and b, Van Veen et al '81].

Gas platelets are metastable structures; annealing to temperatures $>0.3T_m$ allows them to collapse, so that a number of small bubbles are formed. The energetic and kinetic considerations explaining this phenomenon have been discussed by Tyler and Goodhew ['83].

By this stage of bubble growth, the pores are sufficiently large to be imaged in the TEM. As a result far more is known about the following mechanisms of growth.

The equilibrium shape of a bubble may be derived from
thermodynamic considerations, i.e. it is the shape which has the lowest free energy. Bubbles may not always assume their equilibrium shape, if atomic kinetics inhibit changes in shape [Goodhew '81]. The free energy $E_i$ of a bubble is readily described by the equation:

$$E = F + F' + Q + \Gamma \ldots 3.32$$

where $F$ is the free energy of the gas, $F'$ the free energy of a crystal without the bubble, $Q$ the elastic strain energy stored in the lattice because the bubble is present and $\Gamma$ is the total surface energy associated with the bubble [Nelson et al '65]. The equilibrium gas pressure inside a spherical bubble of radius $r$, with isotropic surface tension $\Sigma$, is given by:

$$p_{eq} = \frac{2\Sigma}{r} \ldots 3.33$$

In turn surface tension can be expressed in terms of surface free energy $\gamma$;

$$\sigma = \gamma + A \frac{d\gamma}{dA} \ldots 3.34$$

where $A$ is the surface area and $d\gamma/dA$ describes the change in surface energy as a result of elastic strain. If elastic strain is negligible around the bubble, because atomic relaxation is easy (e.g. at high temperatures $T>0.5T_m$ in crystalline metals), equation 3.32 reduces to $\sigma=\gamma$. In practice values for $d\gamma/dA$ are not readily available, so the assumption that $p_{eq}=2\gamma/r$ is commonly made.

Bubble shape is influenced by the fact that $\Gamma$ in equation 3.32 is given by;

$$\Gamma = \sum_i A_i \sigma_i \ldots 3.35$$

where the subscript $i$ refers to individual planes on which bubble
facets may lie. In the absence of elastic strains this reduces to;

$$\Gamma = \sum A_i \gamma_i \quad \ldots \ldots \ldots 3.36$$

Clearly in an isotropic medium the summation over planes is unnecessary and the equilibrium bubble shape will be a sphere. In crystalline metals surface energy is not isotropic. In such cases, the equilibrium shape is deduced by plotting the $\gamma_i$'s and applying a Wulff construction (for examples and applications see reference Goodhew '81).

It should be appreciated that at least surface diffusion must be possible if bubbles within metals are to change shape. As a result bubble shape changes are only permitted at temperatures in excess of $-0.3T_m$, because below this temperature atomic mobility is extremely low. This means that in addition to bubble shapes being frozen, bubble growth can only occur via athermal processes (see section 3.5.3). At temperatures between $-0.3T_m$ and $-0.5T_m$, vacancy migration through the bulk solid is negligible but surface diffusion processes take place allowing shape changes and growth via migration and coalescence. Above $-0.5T_m$ the number of vacancies in the bulk increases, as does their mobility. This means that at high temperatures, vacancies allow bubbles to change both size and shape.

It is only in the highest temperature regime therefore, that bubbles may be able to shrink or grow to obtain their equilibrium size. Under such conditions their facets will favour the planes of lowest free energy. Under all conditions kinetic factors are likely to influence these processes. Bubbles have usually been observed in
non-equilibrium conditions, because equilibration requires the movement of a large number of atoms over considerable distances. An important consideration is that of the segregation of impurities to the surface of bubbles. For example the formation of oxide, silicide and carbide layers is thought to reduce the surface free energy of certain planes with respect to others [Goodhew '81]. A related effect is the poisoning of a surface so that it has a reduced ability to emit or receive vacancies. Clarebrough et al ['67] suggested that this effect manifests itself in copper when oxygen is present.

The factors mentioned in the paragraph above suggest that surface energies gained from bubble shapes cannot be taken as reflecting the properties of the metal. The deviation of a bubble from its equilibrium shape is a useful piece of information, as it indicates the magnitude of kinetic or surface compositional effects. These effects require monitoring, as they will also play a part in bubble mobility and growth (see section 3.5.2).
4 Blister Formation.

4.1 Introduction.

The introduction of increasing numbers of atoms during ion implantation causes the target material to swell. When doses in excess of $5 \times 10^{17}$ ions cm$^{-2}$ are used, deformation of the target surface is often observed. If the projectile ions are insoluble gases, this deformation takes the form of blisters or pitting. The mechanism of blister formation is not fully understood, although the factors which are probably involved have been described in a large number of publications. The critical dose for blister formation, $\Phi_c$, often corresponds to the dose at which the target is saturated with gas. As the implant dose is increased above $\Phi_c$, blisters sometimes rupture and surface flaking occurs. At very high doses surface erosion becomes significant and results in a pitted topography [Breits and McCracken '73]. The development of surface topography as a result of gas ion implantation has been discussed in detail by Scherzer ['85].

The purpose of this chapter is to present the mechanisms by which blister formation is thought to take place and to describe ways in which blistering may be different for amorphous and crystalline targets.
4.2 Implantation Parameters which Influence Blistering

It has already been mentioned that implant dose affects blistering, however several other factors are also important:

(a) **Target Temperature.**

Erents and McCracken ['73] undertook 36keV helium implants into molybdenum at various temperatures. They established that the following trends exist for a particular implantation dose;

(i) Circular blisters form at room temperature, with some exfoliation.
(ii) At slightly elevated temperatures (~800K) much more exfoliation was noted.
(iii) Intermediate temperatures (~1100K) produced an increased number of complete large blisters.
(iv) High temperatures (~1600K) led to surface pitting.

When dealing with metallic glasses, experimental conditions are limited to low temperatures so that crystallisation is avoided (most metallic glasses have a crystallisation temperature ($T_x$) well below 1000K). However, in chapter 7 the results helium induced blister formation on amorphous CuZr will be presented. They indicate the possibility that amorphous alloys behave in ways similar to heated crystalline targets during implantation.
(b) Implantation Rate.

One way in which the rate of implantation can affect blister formation is through the rate at which energy is deposited into the target surface. If we assume the bulk target thermal conductivity to be high, the overall temperature of a specimen will not be greatly increased by implantation (temperature increases in the region of 50 or 100K might be expected for 100 keV implantation). However, blister formation involves a thin layer of metal losing contact with the bulk of the specimen. After blistering, the rate at which energy is removed from the blister lid may be relatively low. It has been suggested that at high rates of ion implantation (perhaps above \(-5\times10^{13} \text{ ions cm}^{-2}\text{s}^{-1}\)), blister lids may be heated through several hundreds of degrees because of this effect Behrisch et al. ['70] for example, noted sudden large increases in the surface temperature of specimens at blister doses.

Another effect which may result from high dose rates is an increased instantaneous density of gas atoms in the implantation layer. That is, if diffusion of gas atoms out of this layer occurs at approximately the same rate regardless of dose rate, a higher gas arrival rate will mean a greater local concentration of gas at any moment in time. This would lead to a higher rate of gas bubble nucleation (see section 3.4) so that blister formation would occur at a lower dose, and \(\phi_c\) would be reduced. Verbeck et al. ['74] showed that \(\phi_c\) decreases with increasing dose rate. Das and Kaminsky ['74] reported that higher densities of large blisters occurred at higher dose rates, during 500keV helium implants of vanadium and niobium at 1173K.
(c) Implantation Energy ($E_0$).

As already described in section 3.2 the projected range ($R_p$) of implanted ions increases with increasing values of $E_0$. Above $E_0 \sim 100$keV the thickness of blister lids ($t_b$) has been shown to correspond closely to the value of $R_p$. Intuitively we might expect such a result, because the maximum swelling will occur where most implanted atoms come to rest. Below $E_0 \sim 100$keV $t_b$ becomes increasingly more than $R_p$ (see fig.4.1). Possible explanations for this anomalous observation will be presented later in section 4.3.

Blister diameter ($d_b$) also varies with $E_0$. The spread of $d_b$ values produced during particular experiments is often great, but the following relation between $d_b$ and $t_b$ is generally observed;

$$d_b \propto t_b^m, \quad 0.85 < m < 1.5 \quad \ldots 4.1$$

An associated effect is the increase in $\Phi_c$ with increasing $E_0$. This result can be readily explained in a qualitative way. $R_p$ increases with energy, so $t_b$ increases with energy. The implanted gas will therefore be required to deform a greater thickness of material as $E_0$ increases.

The depth over which gas is distributed within the specimen will also increase with $E_0$. Assuming this to be the major factor influencing the variation of $\Phi_c$ with $E_0$, the following relationship is expected to hold;
Fig. 4.1. Blister lid thickness ("Deckeldicke") as a function of helium bombardment energy for Nb at room temperature. Line is the mean projected range ($R_p$).

Fig. 4.2. Interbubble fracture mechanism; a). high density of overpressurised bubbles (pressure a function of depth), b). crack formation, c). gas released from adjacent bubbles, pressure increases, d). crack widens, e). penny shaped crack extends, f). dome shaped blister.
as suggested by Evans ['78]. The relationship has been experimentally verified by Risch ['78].

Factors which affect blister formation may also be introduced before irradiation takes place. For example, the presence of surface roughness (perhaps produced by mechanical abrasion) can delay blister formation. $\Phi_c$ will be higher for rough specimens than smooth ones. This effect has been demonstrated by Sone et al ['77] for molybdenum bombarded with 100keV helium ions to a dose of $10^{18}$He$^+$cm$^{-2}$. after; (a)electropolishing, (b)scratching with #1200 emery paper and (c)scratching with #400 emery paper. The prevention of blistering by surface roughening may occur because no continuous layer of gas can form below a scratched surface. Mechanical polishing is known to introduce structural modifications to a relatively thick (~1μm) layer; this may also contribute to the inhibition of blister formation.

The presence of an oxide layer at the specimen surface might also be expected to influence blister formation, by providing a trapping region for inert gas atoms, or a region of enhanced bubble nucleation. Such a discontinuity in specimen composition may provide a weak interface at which a blister lid may form. This point will be mentioned again when observations of anomalously thin blister lids, made during this project, are discussed in section 7.
As described in chapter 3 low doses of inert gas ions \(10^{15-10^{17}} \text{ions cm}^{-2}\) induce bubble formation. It is therefore reasonable to assume that blister formation, which takes place at higher doses, is associated with the existence of a layer of bubbles. Models of blister formation which rely on such developments constitute the first mechanism to be considered in the next section. They are usually referred to as "interbubble fracture models".

Another proposed model which could account for blister formation is termed the "lateral stress" model. It is based on the fact that implantation causes the specimen to swell, and so induces lateral compressive stress. An analogous situation occurs when thin films are deposited on a substrate. The problem of such films buckling away from their substrates is well known.

In this section the general concepts behind the two mechanisms outlined above will be presented.

(a) The Interbubble Fracture Mechanism

The major developmental contributions to this theory were made by Evans et al [Evans '76,'75,'77]. It is first assumed that layers of overpressurised bubbles form during the initial stages of implantation. The term overpressurised means in excess of the value \(\frac{2\gamma}{r}\) (see equation 3.30). These layers, considered collectively,
exert a perpendicular force on the material to the surface side of their position. In order to quantitatively assess this model Evans et al made the following further assumptions:

(i) The lateral stress caused by bubbles is homogeneously distributed through the material between the bubbles and the specimen surface.
(ii) The bubbles constitute a cubic array.
(iii) All bubbles are of the same radius and internal pressure.

Following these assumptions, the value of internal pressure needed to cause the material to fracture and hence blisters to form is given by:

\[ p = \sigma_f \left[ \left( \pi r_b^2 C_b \right)^{-1} - 1 \right] + 2\gamma/r_b \]

\( C_b \) is the bubble density and \( \sigma_f \) is the material fracture stress perpendicular to the bubble layer. The process of gas bubble induced fracture is schematically presented in fig.4.2. The fracture leads to a crack forming through the bubble containing region, parallel to the specimen surface. Gas is released into the cavity produced. When sufficient gas is in the cavity the material above will be deformed upwards. The condition at which cavity pressure is sufficient to induce deformation is [Das and Kaminsky '76];

\[ p = \frac{16\sigma_y t_b^2}{3d_b^2} \]

\( \sigma_y \) is the yield stress of the blister lid material, \( t_b \) and \( d_b \) are the blister lid thickness and diameter respectively. As mentioned in section 4.2 some discrepancy exists between the implanted range \( R_p \) and the value of \( t_b \) at energies below \( \sim 100\text{keV} \); the experimentally observed values being greater than
the expected ones (see fig. 4.1). This anomaly may be partly explained by the fact that swelling occurs during ion implantation, i.e. swelling in the material of the blister lid may be partly responsible for these observations. However, Evans has suggested that some of this discrepancy may be caused by the most overpressurised bubbles forming at depths greater than \( R_p \). To explain this suggestion we must recall that the majority of the damage done to the specimen will occur closer to the surface than the value of \( R_p \) (see fig. 3.3). This damage provides some vacancies, which aid bubble growth. Bubbles forming at depths greater than \( R_p \) will not receive damage induced vacancies and so (under conditions where the equilibrium concentration of vacancies is low), they must grow by the loop punching process described in section 3.5.3. Loop punching is a less efficient mechanism for reducing bubble pressure than vacancy accumulation, therefore the bubbles with the highest internal pressures may form at depths greater than \( R_p \). As a result the condition for fracture, provided by equation 4.3, is more likely to be fulfilled beyond \( R_p \).

(b) The Lateral Stress Mechanism

During thin film deposition experiments, it is often observed that the specimen buckles upwards, separating from its substrate. It has also been noted that this occurs only after the specimen thickness becomes greater than a certain critical value. This phenomenon is induced by lateral stress within the deposited film. Moreover, the fact that thin films do not buckle whilst thicker ones do, indicates that separation from the substrate depends on the
integral of lateral stress over the specimen thickness.

Eer Nisse and Picraux ['77] applied the lateral stress model to blister lids. They considered lids to be fixed at the edges, and only weakly connected to the underlying material (perhaps as a result of a bubble containing layer). These assumptions allowed the derivation of the following condition for blister lids to buckle upwards:

\[
d_b^2/t_b^3 = KE/[2.5 \times 10^{-4} (1 - p^2) \sigma_y]
\]

and \( t^* \) were considered the most probable blister lid diameter and thickness respectively. \( E, p \) and \( \sigma_y \) are: Young's Modulus, Poisson's ratio and Yield Stress for the lid material. The geometric factor \( K \) varies from 1.4 (for a lid which is unattached at the edges), to 4.9 (for a lid with firmly attached edges).

Experimentally the relationship between the dimensions of the blister lid has been found to obey equation 4.1. This result supports the theoretically derived equation 4.5, and so lends support to this model.

An important component of this model is the existence of a weakened interface beneath the blister lid. Eer Nisse and Picraux have emphasised the fact that the existence of bubbles is only one possible source of this interface. They visualised it forming through stress relaxation at any source of stress concentration. Possible sources of such concentrations are; bubbles, voids and second phase particles. Eer Nisse and Picraux did not assume the existence of bubbles during their calculation of the stress induced; instead they attributed a finite amount of swelling to each atom introduced to the target. The integrated lateral stress need not
exceed the yield stress of the material at the particular depth value equal to \( R_p \). It has been suggested that the lack of agreement between \( R_p \) and measured values of \( t_b \), below 100keV, justifies belief in the lateral stress model of blister formation. However, a quantitative evaluation of lateral stress due to swelling has not been performed, so it is difficult to predict exactly where fracture might occur for a particular set of experimental conditions.

It is difficult to decide which of the two mechanisms described above is responsible for blister formation, because the accuracy with which experimental data can be collected is insufficient to differentiate between them. It seems likely that both will contribute to the overall process and that the extent to which one dominates is the true matter in question.

It is important to note that at temperatures of the order of \( 0.5T_m \) large faceted bubbles have been observed to grow. For example in niobium between 800 and 950°C helium implantation has resulted in bubbles between 25 and 150nm in diameter [Bauer and Thomas '73, Das and Kaminsky '73, Aitken et al '73]. The melting point of niobium is 2420°C. Under these conditions surface deformation may result from the presence of large bubbles near the surface. Thus blister formation takes place as an extension of bubble growth. Later in this thesis the results of helium induced blister formation on amorphous CuZr at room temperature will be described. The results will prove comparable with those seen in crystalline metals at elevated temperatures.
4.4 Saturation and Sputtering

4.4.1 The Saturation Process

The probability that an incident ion will become trapped in the target \( P_t \), is usually derived from thermal desorption spectroscopy. In this technique a known amount of gas is directed at the target, subsequently the trapped gas is released by annealing. \( P_t \) is then evaluated from the ratio of the evolved number of gas atoms \( n_t \) to the dose applied \( n_i \). It has been observed that as the dose increases \( P_t \) decreases continuously towards zero. Eventually a saturation value of \( n_t \) is reached [Webb '80]. Examples of results demonstrating this behaviour in niobium are contained in fig.4.3.

\( P_t \) appears to approach saturation in a near-exponential fashion. Good fits to experimental curves can be obtained by assuming the presence of saturable traps within the target. However, modelling entrapment on this basis is not acceptable because under most conditions bombarding ions create their own traps to some extent (see section 3.2). Two primary modes of saturation can be envisaged:

(i) The target structure receives more gas than it can physically constrain. Saturation caused by this process would be accompanied by bubble and blister formation, with
Fig. 4.3. Trapping of $^3$He ions in a Nb single crystal for different energies implanted to different doses in random directions. The arrows give the critical blister dose.
gas release occurring as blisters burst.

(ii) The specimen is sputtered by the incident ions at a high rate, so that the surface recedes and gas is released.

Erents and McCracken ['73] have pointed out that blister formation provides the major source of saturation during light element implantation, e.g. for helium. Light ions such as helium create little damage in the specimen, cause little sputtering on the surface and penetrate the target to relatively large depths. For heavier ions such as argon, the sputter yield and hence the rate of surface recession becomes significant. As a result mechanism (ii) is more likely to be the dominant saturation process.

Theoretical analysis of the sputter mechanism of saturation was first pursued by Carter et al ['62] on the basis of the surface recession rate \( v; \)

\[ v = \frac{JS}{N} \quad \text{.....4.6} \]

Here \( J \) is the dose rate in ions per unit area per second, \( S \) is the sputter yield in ions per atom, and \( N \) is the atomic density of the target. If we introduce the probability of gas ions stopping a distance \( x \) from the surface \( \eta(x) \), then the rate of gas accumulation at a distance \( x \) from the initial surface is;

\[ \frac{\partial n_x}{\partial t} = J\eta(x - vt) \quad \text{.....4.7} \]

Changing co-ordinates to \( \xi = x - vt \), and calling the maximum implant range \( L \), we can see that;

\[ \eta(\xi)d\xi = 0 \quad \text{for} \quad \xi > L \quad \text{.....4.8} \]

\[ \eta(\xi)d\xi = 0 \quad \text{for} \quad \xi < 0 \]
The total amount of gas trapped up to \( L \) is given by;

\[
N_T = J \int_0^L \int_0^t \eta(\xi) \, d\xi \, dt
\]

.....4.9

When the target surface recedes beyond a distance \( L \) from the original surface, saturation is reached because the rate at which gas is trapped equals the rate at which surface erosion releases gas. Carter and Colligon ['68] have shown that this results in a gas concentration at saturation of;

\[
N_s/n = \eta R_p/SL
\]

.....4.10

where \( N_s \) is the saturation gas content, \( R_p \) the mean projectile range, \( n \) the number of target atoms between the surface and \( x=L \). The maximum gas content occurs when the surface recedes past the maximum range for implanted ions. This fact will be used in section 7.2.4, where the results of argon implantations of amorphous CuZr are displayed for this project.

4.4.2 Sputtering.

The fact that light atoms produce a lower sputtering yield than heavy ones has been mentioned in the previous section. However, the sputtering mechanism is more complex than this statement reveals. Details of the variation of sputtering yield with atomic number of projectile ion, and for several targets, are given in fig.4.4. There is clearly a periodic behaviour to this parameter.
Fig. 4.4. Variation of sputtering yield with atomic number of the bombarding ion for 45keV bombardment of Cu, Ag and Ta targets.
Sputter yield also has a relatively strong dependence on the angle of incidence for the ions concerned. Molchanor and Tel'kovskii ['63] discovered the approximate relation;

\[ S_\theta = \frac{S_0}{\cos \theta} \]

where \( S_0 \) is the yield at normal incidence, when studying 25keV Ar\(^+\) bombardment of copper. Their results were gained near normal incidence. It seems that maximum yield is obtained at angles of 40-80° to the normal, after which yields decrease again.

A further complication, as far as this project is concerned, is that little is known about the sputtering of alloys [Carter and Colligon '68]. What experimental evidence exists reveals little in the way of significant trends. In the case of binary alloys the development of a modified surface layer, enriched in one alloy component (with respect to the original alloy), has been observed [Wehner '58, Asada and Quasebarth '29]. This suggests that one component is sputtered in preference to the other, so that a layer forms which is depleted in the preferred element. After a short period of sputtering, an equilibrium situation must exist, as analysis of the sputtered atoms indicates a ratio close to the composition of the bulk alloy [Wehner '58, Wolsley et al '64]. The existence of preferential sputtering rates, and the extent of the resulting enrichment will vary greatly from alloy to alloy [Webb '86]. The phenomenon must be related to one particular factor, about which little is known, the relative surface binding energy of atoms in an alloy. Further contributions to the effect will be made by; the relative collision cross sections of the constituents, and the maximum
energy which can be transferred to each.

The sputtering effects discussed here will be mentioned again when experimental results concerning high energy (80keV) argon implants and ion beam milling (~5keV) are discussed in sections 7.2.2 and 7.2.1 respectively.
5.1 Introduction.

The scope of this chapter is necessarily wide, because a large number of experiments have been performed, but few have involved similar targets or conditions. Indeed, the great diversity of amorphous alloys systems has provided a problem for those trying to understand the effects of radiation damage in them. There is no reason to assume any two amorphous alloys will respond to radiation damage in the same way. The large number of alloys, and range of conditions that have been studied means recognising behavioural trends is difficult.

Most emphasis will be placed on experiments involving inert gas ions as the bombarding projectiles, as these will be directly relevant to this project. However, the results of heavy ion, electron and neutron bombardment will also be presented here, because similar damage processes are involved. Reviews on this subject have been published by Grant ['81] and Nandedkar and Tyagi ['84]. The most recent review of ion implantation of metals was published by McHargue ['86].
5.2 The stability of Amorphous and Crystalline Phases during Irradiation

During irradiation a considerable amount of energy may be introduced to the target structure. It is not surprising therefore, that crystalline structures have been observed to transform and that amorphous phases have been seen to crystallise. However, before the nature of irradiation damage is fully considered it is surprising to find crystalline structures transforming to metastable crystalline and even amorphous structures. The first reviews of literature discussing the effects of implantation on metallic structure were made by Meyer ['80], Poate and Cullis ['82], Grant ['81] and Sood ['82].

At this time it was recognised that ion implantation and electron bombardment could cause metastable crystalline phases to be produced at low doses. Also, amorphous phases had sometimes formed at high doses. However the available data was limited and the evidence appeared somewhat conflicting. Over the past few years many more investigations have been performed [McHargue '86, Brimhall and Simonen '86, Parkin and Elliot '86, Pedraza and Mansur '86] and qualitatively the processes concerned with phase stability during irradiation are better understood.

Cascades produced by ion implantation (see section 3.2) may involve $10^3$ to $10^6$ atoms, and last $\sim 10^{-11}$s. It has been estimated that the effective quench rate following cascade formation may be $\sim 10^{14}$Ks$^{-1}$. Clearly the residual damage
structure is responsible for observed phase transformations. The magnitude of the damage introduced is a starting point, from which the kinetics of relaxation lead to defect annihilation and hence the final structure. The amount of damage created will be determined by the energy of the incoming particle and it's mass relative to the target atoms (see equation 3.1). As an example of the second factor we can compare electron and ion bombardment. An electron creates fewer point defects than a heavy ion implanted with the same energy. This is worth noting when considering the literature on irradiation induced phase changes, as the results of electron and ion bombardment are often compared. It explains why some targets can be made amorphous by ion bombardment but not electron bombardment.

During cascade collapse, the factors which aid metallic glass formation during rapid quenching of the melt will play a part in the possible irradiation induced transformation. For example Brimhall and Simonen ['86] have proposed that the irradiation induced transformation to the amorphous phase is favoured by a restricted range of solubility in a compound (i.e. intermetallic or line compounds). This situation demands that a particular stoichiometry must be achieved before the equilibrium phase is produced. It thus requires more atomic diffusion than the case where a wide range of compositions are soluble.

Initially the transformation can be considered energetically, i.e. it occurs when the free energy of the crystalline phase is increased beyond that of the amorphous phase by the introduction of defects and extra atoms. Relaxation of this structure (perhaps back to the equilibrium phase) depends on atomic mobility. It has been
stated that alloys which readily form amorphous phases are subject to a rapid increase in viscosity, with falling temperature, near their melting point. This indicates a limited atomic mobility which may prevent crystal formation.

Pedraza and Mansur ['86] have suggested a new defect complex which may provide a route to amorphisation. The motivation for proposing this defect comes from the fact that generally a large number of irradiation induced point defects are annihilated when the cascade collapses. Also, in pure metals and most alloys atomic mobility is sufficiently high, following cascade formation, for the aggregation of like point defects to occur. This results in dislocation formation. For intermetallics no such dislocations are observed. Pedraza and Mansur attribute this observation to the fact that a new defect, consisting of a vacancy and an interstitial, is stable in these alloys. Further, they have hypothesised that such defects are stable because although the intermetallic exhibits long range order, sites with short range order are available to stabilise the position of the displaced atom. The vacancy produced then serves to relieve stress through relaxation about the interstitial. In this way both defects would be retained by the lattice. Pedraza and Mansur applied this model to the electron induced amorphisation of NiTi and showed that it successfully predicted the dependence of the critical dose for amorphisation on temperature.
5.3 Inert Gas Ion Implantation of TM-M Glasses.

Like the following four sections this one will be a review based on a table in appendix A.1. The discussion presented here will draw upon this appendix and provide a general view of how inert gas ion implantation affects the microstructure of TM-M glasses.

In the low energy region of ion implantation (5-100keV), at room temperature, the development of inert gas bubbles has been observed on several occasions. Bubbles first develop after doses of about $5 \times 10^{16} \text{cm}^{-2}$ have been applied. Reports suggest that the mean bubble size increases with dose thereafter [Van Swijgenhoven et al '82, Carter and Grant '81]. This behaviour is not observed in crystalline metals at room temperature. Experiments in Ni, Mo and Nb produced a saturation of bubble size with dose. For the crystalline metals athermal bubble growth is limited by the need to create interstitial loops (see section 3.5.3). Clearly athermal bubble growth in TM-M glasses is subject to a lower energy barrier than that of loop punching. This observation suggests that local atomic rearrangements are much easier in the glass than the crystal. The development of bubble growth equations via loop punching mechanisms is well described by Evans ['77]. Bubble growth as a function of dose is found to have a $1/r^2$ dependence.

In crystalline systems elevated irradiation temperatures are known to aid bubble growth through the increased mobility of point defects. However Van Swijgenhoven et al ['84] failed to find a trend for bubble growth in a glass as the temperature of irradiation
Fig. 5.1. Van Swijgenhoven's data for bubble size versus implantation temperature.
was increased. Their results are displayed in fig.5.1. Although no explanation of these results was attempted by Van Swijgenhoven et al, the results of experiments performed during this project indicate why such a lack of clear temperature dependence may occur under the conditions applied.

Considerable differences in bubble size have been noted for helium and argon implantations performed under otherwise identical conditions [Grundy '83, Nanao '81, Tyagi '84]. As has already been suggested athermal bubble growth is relatively easy in metallic glasses. The differences in bubble size between these gases can partly be explained by their equations of state, i.e. for a given number of atoms in a given volume the pressure would be higher for argon than helium. A further influential fact is that for a given energy argon ions have a lower range than helium ions. The density of gas atoms in the metal is therefore highest for argon if the two gases are implanted at the same energy, and to the same dose.

At high doses (greater than ~ 2x10^{17} cm^{-2}) helium ion implantations cause blister formation. The critical dose increases with energy of implant, as shown in fig.5.2, and is of similar magnitude to that of crystalline metals. The mechanism of blister formation is less decided than for crystalline metals however, because athermal bubble growth appears to be easier. This would suggest that bubbles are subject to lower internal pressures in glasses. If this is true the pressure required for blister formation by interbubble fracture is less likely to be achieved. Some calculations indicating whether interbubble fracture could be responsible for blister formation will be performed later in this
Fig. 5.2. Critical blister dose plotted against incident ion energy.

Data was collated from the indicated publications and refers to a number of different amorphous alloys.
thesis. An alternate way in which blisters could form would be the continued growth of bubbles with dose, followed by coalescences near the surface. [Nandedkar and Tyagi 1981b, Van Swijgenhoven et al 1983a].

Some anomalous blister observations have been made on metallic glasses. In particular Nanao et al ['81] observed blistering and flaking to occur at two depths into the specimens. A similar result was seen in crystalline metals by Jones and Johnson ['87] and was said to provide evidence for the lateral stress mechanism of blister formation. Van Swijgenhoven et al ['82] observed large blisters of low areal density following 5keV argon implants at 45° to normal incidence. This is surprising on two counts: (i) the density of blisters was much lower than observed on crystalline metals, (ii) argon ions usually produce surface pits rather than blisters because material is rapidly sputtered from the specimen surface by heavy ions. The second factor is particularly important at 45° (see section 4.4). More evidence for the development of surface porosity under argon irradiation exists than for blister formation [Nanao '81, Tyagi et al '83 and '84]. Two explanations for blister formation under low energy argon bombardment can be proposed:

(i) An oxide layer forms on the specimen surface, so that a weakened interface develops between oxide and metal. Evidence for substantial knock-in can account for oxide formation at the surface of bubbles in aluminium [Cox et al '84].

(ii) The sputter yield of the metallic glass could be significantly lower than expected so that blister formation occurs before the surface
can be eroded very far. Emmoth et al ['81] measured sputter coefficients for a Fe_{40Ni_{40}B_{20}} metallic glass implanted with 2 to 20keV helium ions. They concluded that the sputter yield was at least three times lower for their specimens than for Inconnel stainless steel, iron and nickel. However, later in this thesis an estimate of the sputter coefficient for 80keV argon ions incident on a CuZr glass will show a similar value to coefficients for copper and zirconium.

Some attempts to study structural changes under inert gas ion irradiation have been made. X-ray diffraction studies revealed little or no change [Schumacher et al '80, Hayashi et al '83b, Ayano et al '79]; changes that were observed indicated an increase in contained free volume and/or a decrease in structural order. More dramatic changes were observed in some TEM studies, where partial crystallisation had occurred. Hayashi et al found that their specimens crystallised during implantation with helium ions. Their experiments were performed at elevated temperatures (400°C) which would have aided radiation induced crystallisation. However, identification of the resulting phases indicated that they were not the equilibrium ones. Clearly implantation changed the mode of crystallisation; the mechanisms behind this change are not clear but the following factors may have been influential:

(i) Increased diffusion rates of point defects.
(ii) Dislocation networks developing during crystallisation as a result of radiation damage.
(iii) The presence of gas atoms in the crystals.
(iv) The introduction of oxygen atoms.
Points (ii) and (iii) would both impose stresses within a crystal, and so affect the structure that formed.

5.4 Inert Gas Implantation of TM-TM Glasses.

Far fewer implantations have been performed on TM-TM glasses but observations suggest their behaviour to be qualitatively similar to TM-M glasses. Inert gas bubble and blister formation seem to take place after approximately the same doses as other metals and once again bubbles grow larger for argon than for helium implantation. [Tyagi et al '81 and '84, this thesis]. Tyagi et al ['84] did suggest that the glasses $\text{Ni}_{60}\text{Nb}_{40}$ and $\text{Ni}_{64}\text{Zr}_{36}$ showed a greater resistance to blister and flake formation than other glasses. They also noted that these remained amorphous during 50 to 150keV helium and argon ion bombardment, while amorphous $\text{Ni}_{33}\text{Zr}_{67}$ became partially crystalline.

5.5 Heavy Metal Ion Implantation of Metallic Glasses.

Studies involved with this type of experiment generally involve 'self-ion' bombardments, i.e. the use of one of the alloy components as the implanted species. As a result a great deal of displacement damage can be created, but modifications to the microstructure are not influenced by chemical differences between implanted and host atoms. Some discussion of this topic has been pursued in section 5.2 on phase transformations and examples of work in this field are contained in appendix A.3.
5.6 Electron Bombardment of Metallic Glasses.

The analysis of results obtained during the electron bombardment of metals is complicated, because two processes could be responsible for structural modification. Firstly, electrons are capable of displacing atoms from their original sites if they enter the specimen with sufficient energy. However, the energy transferred to a displaced atom is usually quite small because electrons have a low mass (see equation 3.1), so the self-annihilation of defects after damage at room temperature is relatively frequent. In metallic glasses such annihilations have been demonstrated by positron annihilation studies, as described in section 3.3. Secondly, electrons lose energy by a number of processes as they pass through a material. This leads to specimen heating. Most experiments using electrons to damage specimens have been performed in transmission electron microscopes, where microscopic changes can be imaged by the beam transmitted through a thin specimen. Beam heating as a result of electron energy losses is a phenomenon well known to electron microscopists. Estimates of specimen temperatures in the electron beam indicate that rises of 50 or 100K are not uncommon.

Several groups have reported phase changes in amorphous metals subjected to electron bombardment [Barbu and Limage '83, Brimhall '84, Doi and Imura '80]. The results generally indicate that electrons do not affect crystal growth rate or morphology but that they do increase the rate of nucleation. There is little doubt that an electron beam increases atomic diffusion coefficients, and thereby aids nucleation. Whether the major contribution to diffusion is caused by the atomic displacements or beam heating has yet to be established.
An interesting paper was published by Audouard et al ['82] who calculated the number of recombinations occurring after electron bombardment at 21K, for amorphous and crystalline Fe$_{75}$B$_{25}$. Their results suggested twice as many displacements remained in the crystal than in the glass, further lending support to the theory that local atomic rearrangements occur more easily in the glassy state. Among their assumptions Audouard et al took the displacement energy in the two states of the the alloy to be identical. This is probably a reasonable assumption because metallic bonding occurs in both and the difference in density is only of the order of 1%.

The effects of exposing the amorphous CuZr alloy to the electron beam will be described later in this thesis. They were of interest because an analytical electron microscope was used to study the alloy before and after inert gas ion implantation.

5.7 The Irradiation of Metallic Glasses with Neutrons.

Studies involving the neutron bombardment of materials are particularly important to the nuclear industry as they can closely simulate some of the conditions imposed on internal reactor structures. Appendix A.5 contains references describing the neutron bombardment om metallic glasses. There has been no recorded observation of neutron induced crystallisation. However, several reports of structural modifications on the atomic scale have been made. Examples of such changes have been detected using X-ray diffraction patterns [Cline et al '83, Doi et al '79, Kramer and Johnson '79], electrical resistivity measurements [Audouard et al '79, Takamura and
Kobiyama '84], specimen ductility [Cline et al '81], DSC [Cahn et al '81, Doi et al '79] and positron annihilation [Audouard et al '83]. Each method used suggests that neutron irradiation increases the amount of disorder present in the structure. Such results have even led to the proposal that metallic glasses may provide 'self-regenerating' materials in environments where they are subject to high fluxes of radiation [Megusar et al '84].

5.8 Modelling Bubble Growth in Metallic Glasses.

It is generally accepted that the nature of collision cascades in metallic glasses is quite similar to that in crystalline metals [Doyama '81, Krishan '82] unless the orientation of the crystal to the incoming particles is such that significant channelling occurs. The number of displaced atoms and the time period for energy dissipation should only be insignificantly different. However, the number of defects that remain after cascade collapse is expected to be lower in the glass because local atomic rearrangements are easier [Audouard et al '82]. Despite this bubbles grow faster at room temperature in glasses than in crystalline metals indicating that growth is not limited by 'athermal' mechanisms such as loop punching.

Only one attempt has so far been made to quantitatively model bubble growth in metallic glasses. Van Swijgenhoven et al ['83] published work in which they attempted to explain helium bubble growth in amorphous FeNiMoB after 5keV implantations. The development of their model will be followed here, so that the assumptions made can be compared with the more basic
assumptions applied later in this thesis. Although the model described later is less complex than that presented by Van Swijgenhoven et al, the concepts involved allow the results to be compared more readily with experiment. It also conveys the fact that reasonable fits to experimental data can be obtained quite readily if small adjustments are made to the value of parameters which are difficult to measure.

In their model Van Swijgenhoven et al primarily assumed that bubbles will only grow if they are overpressurised so that the attraction of free volume is analytically favoured. The mechanism for bubble growth was then taken to be the accumulation of free volume.

The nature of point defects in amorphous alloys has already been discussed in section 2.4. The implantation of gas ions leads to the formation of extrinsic point defects, which Van Swijgenhoven et al termed "negative free volume" (NFV) and "positive free volume" (PFV) regions. The change in bubble volume resulting from the production of a region of PFV at a distance $x$ from the bubble was defined as $V_p(x)$. Similarly the formation of NFV will cause a decrease in bubble volume which was defined as $V_n(x)$. It was then assumed that because the accumulation of PFV is energetically favoured the amount of PFV reaching the bubble would be greater than the amount of NFV. It should be remembered that in crystalline metals preferential sinks for interstitials are present, so a mechanism exists by which more vacancies can be present in the matrix than interstitials. For amorphous alloys this is not the case, so bubbles only grow through the presence of a surrounding strain field that favours the attraction of PFV. Van Swijgenhoven et al imposed this effect by using the relation:

$$|V_p(x)| > |V_n(x)| \quad \cdots 5.1$$
effectively imposing a difference in "capture length" (ΔL) i.e. the distance from the bubble within which point defects are accumulated, for PFV and NFV. The magnitude of ΔL will of course depend on the strain field around the bubble and hence the pressure within it. The rate of bubble growth was then expressed as:

\[
dV_b/\text{dt} = k(dN/dv\text{dt}) \left[ \int_V (\Delta V_p + \Delta V_n) \text{dV} \right]^\ldots\ldots.5.2
\]

where \( k \) is the defect survival probability (i.e. the probability that a defect pair will not recombine), and \( dN/dv\text{dt} \) is the rate at which atoms are displaced per unit volume. To remove the integral Van Swijgenhoven et al applied the concept of a difference in capture length. They also replaced \( dN/dv\text{dt} \) using the equation;

\[
dN/dv\text{dt} = P(z) \phi \ldots\ldots.5.3
\]

where \( P(z) \) is the number of atomic displacements caused by an incoming helium ion per unit distance travelled. This is of course a function of depth \( z \). \( \phi \) is the dose rate or \( dD/dt \). As a result the following differential equation describing the change of bubble radius with implanted dose was obtained;

\[
\frac{dr}{dD} = ka\Delta L P(x) \ldots\ldots.5.4
\]

with \( a \) being the mean atomic volume of the metal.

Bullough et al ['70] derived several equations describing the interactions between microstructural defects in crystalline metals. The form of the interaction energy between a bubble and a vacancy was said to be;

\[
E_{\text{int}}(r) \propto (p - 2\gamma/r_b)^2/r^6 \ldots\ldots.5.5
\]

where \( r \) is the distance of the vacancy from the bubble, \( p \) is the contained pressure, \( \gamma \) is the surface energy, and \( r_b \) is the bubble radius. If all vacancies are captured within a distance \( r_0 \) of the bubble, and
$E_{\text{int}}(r)$ is assumed constant for $r < r_o$, the following relationship holds;

$$r_0^3 a (p - 2\gamma/r_b) \quad \ldots \ldots 5.6$$

Van Swijgenhoven et al had already defined the capture volume of the bubble as $4\pi r_c^2 \Delta L$ which will be approximately equivalent to the capture volume defined by equation 5.6, i.e. $4/3\pi r_o^3$. They were thus able to imply the following proportionality between $\Delta L$ and the excess pressure in the bubble;

$$\Delta L \propto (p - 2\gamma/r_b) \quad \ldots \ldots 5.7$$

This led Van Swijgenhoven et al to write;

$$dr/dD = \xi_1 (p - 2\gamma/r_b) \quad \ldots \ldots 5.8$$

where $\xi_1$ is a constant of proportionality. By assuming the number of helium atoms reaching a bubble per unit time is proportional to the surface area, ie;

$$dN/dD = \xi_2 r_b^2 \quad \ldots \ldots 5.9$$

and employing an equation of state developed by Mills et al ['80], it was deduced that the change in bubble pressure could be related to dose by;

$$\frac{dP}{dD} = \frac{3}{4\pi r_b^2} f(P, \rho, T) [\xi_2 r_b^2 - \frac{3N}{r_b} \xi_1 (p - 2\gamma/r_b)] \quad \ldots \ldots 5.10$$

In this equation $f(P, \rho, T)$ is an involved function which need not concern us here. It need only be recognised that equation 5.8 and equation 5.10 must be solved simultaneously to describe bubble growth. In fact values of $\xi_1$ and $\xi_2$ were obtained by fitting curves to the experimental data for $dt/dD$. The values obtained were then used to calculate $p$ and $\Delta L$. 
5.8.1 Discussion of the Model.

The results of this analysis suggest that quite a wide range of internal bubble pressures could account for the growth observed. For the smallest bubbles the contained gas could be exerting between 2 and 20 GPa on the surrounding metal. However, this range tells us little about the difference between bubbles in crystalline and amorphous alloys because the lowest pressure (2GPa) would allow bubbles to be at equilibrium, while the highest (20GPa) is greater than that required for loop punching (e.g. in molybdenum [Evans '83]). These comparisons leave some doubt as to the usefulness of applying this model. Van Swijgenhoven et al suggest that the 'punching' of interstitials as a result of internal pressure is unlikely to occur. However the ease with which local atomic rearrangements occur in metallic glasses has already been expressed in this thesis. It follows that relaxation of the atomic structure should be relatively easy and will produce the same pressure relieving effect as interstitial loop production in crystalline metals. The process may well have a lower activation energy than loop punching because of the ease with which local atomic rearrangements occur. The activation energy will certainly be less well defined because of the variation in atomic separation characteristic of the amorphous structure.

The growth of bubbles in the amorphous structure requires the accumulation of free volume, however there is no evidence to suggest crystallisation occurs as a result of bubble growth. Therefore, long range atomic movement does not occur and the structure retains some free volume over and above that present in the crystalline state. It is
possible that the surface of the specimen acts as a source of free volume for the amorphous matrix, just as it provides vacancies in a crystal [Marachov et al '87, Cahn '86]. Near surface implantations would then result in near equilibrium bubbles.

From their model Van Swijgenhoven et al calculated values of $\Delta L$ as a function of dose. The results indicated that $\Delta L$ was much greater than the inter-bubble separation [Van Swijgenhoven et al '83a]. Even for the highest doses $\Delta L$ was still of the same order as the distance between bubbles. This means that gas is insoluble in the metal; a fact which was included in the essential assumptions of the model.

Later in this thesis evidence for the coalescence of bubbles within a metallic glass will be presented. Indeed the experimental results of Van Swijgenhoven et al support the idea that coalescences occur, because the bubble concentration falls with time of implantation. They have also observed a bimodal distribution of bubble size after implantation to high doses; which also suggests that coalescences had occurred.

In chapter 7 it will be shown that bubble growth in metallic glasses can be explained in part by the following assumptions:

(i) A nucleation period occurs.
(ii) Growth initially occurs by rapid bubble coalescence.
(iii) During implantation and after nucleation gas atoms migrate rapidly to bubbles, i.e. the rate at which gas enters a bubble can be calculated from the dose rate per unit volume and the bubble density according to equation 7.8. It is not dependent on the surface area as suggested by Van Swijgenhoven et al in
equation 5.9.

(iv) Structural relaxation is relatively easy so the gas pressure is given by $2\gamma/r_b$.

(v) The width of the bubble size distribution increases with dose because coalescences occur.

Having considered theoretical and experimental observations that have been reported in the past, it remains to describe the experimental investigations performed during the course of this project. Chapter 6 consists of a description of the experimental techniques employed, while chapter 7 contains the results obtained. Chapter 7 will be divided into sections which consider the following particles bombarding amorphous CuZr: low energy (5keV) argon ions, 80keV argon ions and 100keV helium ions.
6 Experimental Techniques.

6.1 Alloy Production.

Small ingots of a Cu_{50}Zr_{50} alloy were produced in an argon arc furnace. Relatively pure metals were used in the process; 99.99+/-% copper and 99.8+/-% zirconium. Homogenisation was performed by melting, inverting and remelting. The alloy was then rapidly solidified by the process of melt-spinning. Fig.6.1 shows the equipment used. No atmospheric shroud was available so the process was performed in air. For this reason oxidation was expected to prove problematical during later experimental stages. The two surfaces of the melt-spun ribbon will be referred to as the "wheel-side" (which solidified in contact with the copper substrate) and the "air-side" (which was uppermost during solidification).

6.2 The Scanning Electron Microscope (SEM).

The SEM employs back scattered electrons to obtain an image of the specimen surface. Relatively high magnification images can be obtained in comparison to optical techniques. An instrument was available on which an energy dispersive X-ray (EDX) detector had been mounted. The details of EDX analysis in the SEM will not be dealt with here as it is covered in many texts and will not be modified during the course of this thesis. However, the technique is capable of providing the composition of a
Fig. 6.1. The melt spinning apparatus.
specimen in weight percent.

6.3 X-Ray Diffraction.

The fact that X-ray diffraction is commonly used to study amorphous alloys was mentioned in section 2.2. In this project an X-ray diffractometer was used to confirm that the alloy was initially amorphous. It was also used to confirm that the equilibrium crystalline phases formed when samples were annealed above the crystallisation temperature. All data were collected using Cu\textsubscript{K} X-rays.

6.4 Differential Scanning Calorimetry (DSC).

DSC was performed on the melt spun ribbon by Dr G. Gregan of Sheffield University. In this technique the heat flow between the sample and an inert reference specimen of similar mass is recorded, while both are subjected to the same thermal treatment. Metallic glasses have a large enthalpy of crystallisation, so the technique readily indicates the temperature at which crystallisation takes place. Most significant for this project is the fact that DSC traces are affected by the presence of oxygen in the alloy, as described in section 2.5. The traces obtained from each ribbon produced were used to select a sample in which the oxygen content was as small as possible.
6.5 Specimen Preparation for the TEM.

Initially ribbon samples were mechanically polished on both surfaces. The procedure involved #1200 emery cloth, 0.5 and 0.25um diamond pastes. Conventionally 3mm diameter discs are punched for use in the TEM. The specimens punched for this project were approximately 3 by 2.5mm in dimension, because the ribbon was only ~2.5mm wide. An additional problem was that the ribbon was only ~20um thick.

The two techniques available for the final production of thin electron transparent foils were:

(i) Electrochemical jet polishing; in which jets of acid are directed at both sides of the foil and a potential difference applied.

(ii) Ion beam milling; in which low energy (~5keV) argon ions are directed at both sides of the specimen. A low angle of incidence is used, so that displacement cascades occur close to the surface and some displaced atoms obtain sufficient velocity perpendicular to the specimen to escape from the surface.

It is known that ion beam milling modifies the near-surface microstructure of a sample. It will also be shown, in section 7.2.1, that a significant amount of argon can be detected by EDX analysis after the process has been used on amorphous CuZr. These factors led to the use of electropolishing for the preparation of specimens that were to be implanted with argon ions.

The apparatus available for electropolishing was a Struers "Tenupol".
This was used with a slightly modified specimen holder so that discs smaller than the normal 3mm diameter could be thinned. This type of equipment is useful because the following parameters are readily adjusted: electrolyte composition and temperature, applied voltage and the flow rate within the jets. In addition a light sensitive diode could be used to prevent current flowing after perforation had been achieved. The electrolyte used was a 15% solution of nitric acid in methanol, to which small amounts of glycerol had been added to increase the viscosity. The specimens were initially quite thin, and this meant that good polishing conditions had to be achieved very soon after thinning had begun. To help solve this problem the reaction rate was reduced by cooling the electrolyte below 230K. The potential of the specimen was +9V and flow rate was minimised. The electrochemical thinning process involves the formation of an oxide film which is removed by the flow of electrolyte. A polishing film is set up in dynamic equilibrium between the metal and the electrolyte. In the case of zirconium alloys the Tenupol parameters must be carefully set and the electrolyte freshly produced, or there is a tendency for a stable oxide layer to form. In such an event thinning results in a thick layer of oxide forming. The effect is demonstrated in fig.6.2, where copper crystals can be seen embedded in a film of zirconia. This film extends beyond the edge of the amorphous metal. Fig.6.2a is a bright field transmission electron micrograph, while fig.6.2b is a dark field image. Fig.6.2b was obtained by imaging with the inner spots of the diffraction pattern contained in fig.6.3a. This pattern was taken from the thinnest region of the specimen. Fig.6.3b is the diffraction pattern taken from the thicker region and is equivalent to fig.6.3a superimposed on the diffuse pattern associated with amorphous CuZr.

Although specimens were eventually prepared without visible evidence of
Fig. 6.2. Region of amorphous CuZr covered with a film of zirconia containing crystals: a). bright field image, b). dark field image.
Fig. 6.3. Electron diffraction patterns obtained from: a). the film containing crystals, b). the film over the amorphous alloy.
an oxide layer containing copper crystals, it was still considered important to investigate the near-surface nature of the electropolished specimens. The remaining experimental techniques to be described in this section are concerned with this and other analytical experiments.

6.6 Electron Energy Loss Spectroscopy (EELS).

EELS is based on the energy distribution of electrons which have passed through a specimen, some of which will have interacted with atoms or specimen electrons. From a TEM conventional (i.e. serial recording) EELS equipment readily provides qualitative information about the chemical nature of thin samples. The EEL spectrometer used during the course of this project was a VG-ELSSO which was mounted on a Philips 400T electron microscope. A feature of EELS which proved particularly useful is that it can provide reasonably accurate determinations of specimen thickness [Joy '79, Williams '84].

In general the EEL spectrum is divided up into two parts which are known as the "low" and "high" loss regions. A schematic representation of a spectrum is shown in fig.6.4. The zero-loss peak represents electrons which pass through the specimen without being scattered, those which are elastically scattered and those which only lose ~0.1eV through phonon excitations. It is of finite width because:

(i) The electron source has an inherent energy width, caused by slight fluctuations in the accelerating potential and temperature variations at the filament.
Fig. 6.4a. Schematic diagram of an EEL spectrum.

Fig. 6.4b. Quantifying an edge.
(ii) The spectrometer separates electrons according to their energy, by bending their paths in a magnetic field. The resolution of the spectrometer under good conditions is typically 1 to 5 eV.

The low loss region of the spectrum also contains electrons which have undergone plasmon interactions. Plasmons are collective excitations of the conduction band electrons. They can be used to characterise specimens because their frequency and hence their energy is related to the density of free electrons in the specimen \( \left( n_e \right) \). The following relationships hold for the frequency \( \omega_p \) and the energy \( E_p \);

\[
\omega_p = \frac{1}{n_e^{1/4}} \quad \cdots \quad (6.1)
\]
\[
E_p = \hbar \omega_p \quad \cdots \quad (6.2)
\]

where \( \hbar \) is Planck's constant. Typically \( E_p \) is \( \sim 20 \text{eV} \). The mean free path for an electron to cause a plasmon excitation (for electron energies in the 40 to 100 keV range) is between 50 and 150 nm. This means that more plasmons are excited in thicker specimens. A particular electron may cause two, three or more plasmon excitations while passing through a specimen. As a result it will lose \( 2E_p, 3E_p, \ldots, mE_p \) in energy. The probability of exciting a particular number of plasmons is given by the Poisson distribution, i.e.,

\[
P(m) = \frac{1}{m!} \left( \frac{t}{L_p} \right)^m \exp\left(-t/L_p\right) \quad \cdots \quad (6.3)
\]

with \( m=0,1,2, \ldots \). \( t \) is the specimen thickness and \( L_p \) is the plasmon mean free path. This allows us to write;

\[
p(1)/P(0) = t/L_p \quad \cdots \quad (6.4)
\]

where \( p(1)/P(0) \) is the ratio of counts under the first plasmon peak to the number of counts under the zero-loss peak. This equation means that \( t \) can be calculated if \( L_p \) is known. A knowledge of specimen thickness will prove important for the quantitative analysis of specimens.
There are other means of measuring specimen thickness in the TEM, but each have drawbacks which meant they could not be used on implanted specimens; they are:

(i) The convergent beam method, which can only be applied to crystalline samples.

(ii) The contamination spot method, which can ruin valuable specimens and cannot be used easily if there are many features in the field of view.

It is possible to calculate $L_p$ from $n_e$, but for the purposes of this project (where $n_e$ is not known) $L_{pCuZr}$ was obtained experimentally. Thin foils of CuZr were produced and EEL spectra were collected from a number of regions. For each spectrum a contamination spot was created nearby by focussing the electron beam at a very low spot size. Contamination spots are formed when carbon deposits build up on both sides of the specimen. If the specimen is then tilted through a known angle and an image showing clear separation of the contamination layers is recorded the specimen thickness can be determined. The errors which result from this type of measurement were assessed by Rae et al ['81]. For a tilt of $45^\circ$ the specimen thickness is given by:

$$t = \sqrt{2} \ d \quad \ldots6.5$$

where $d$ is measured as shown in fig.6.5. Equation 6.4 was then used to obtain values of $L_p$. The average value of $L_p$ obtained by this procedure for 100keV electrons is presented in section 7.1.3.
Fig. 6.5. An example of a contamination spot at 45° to the electron beam.
In the high-loss region of the EEL spectrum (above ~50eV) characteristic "edges" are seen. These result from electrons which have caused inner-shell ionisations. These edges are superimposed on a smoothly decreasing background. Each successive edge contributes to the background intensity. The background can usually be removed by fitting an equation of the form:

\[ I = AE^{-r} \]  \[ .6.6 \]

to the data on the low energy side of the edge. The constant A and the exponent r both depend on the acceptance angle of the spectrometer (β).

The energy at which an edge begins is the classical ionisation energy of an electron shell; EEL spectra thus offer qualitative information about the composition of the specimen. The number of electrons undergoing a particular ionisation interaction is given by;

\[ I_E = IN_0 \beta \]  \[ .6.7 \]

where N is the number of appropriate atoms in the analysed volume. \( \sigma_\beta \) is the differential cross section for the excitation, which is dependent on E and β. \( \sigma_\beta \) increases as the value of E decreases. Because light elements have lower inner-shell ionisation energies they are more easily detected than heavy elements.

In some cases it is possible to calculate the actual number of atoms which have contributed to an edge. Quantification of characteristic edges is performed using the equation;

\[ N = I_\beta (\beta, \Delta) \sigma(\beta, \Delta)/I_1 (\beta, \Delta) \]  \[ .6.8 \]

This relationship is most easily understood through reference to fig.6.4 where it is shown that: \( I_1 \) is the intensity under the low-loss region and \( I_\beta \) is the intensity in the edge after the background has been subtracted. These parameters must be evaluated over the same collection.
angle and energy window $\Delta$.

For thin specimens ($t<50\text{nm}$) the characteristic edges are sharp and of a shape that agrees well with theory. However, as the specimen thickness increases the number of electrons which suffer multiple scattering during their passage through the specimen increases. As a result edges become increasingly less well defined. A specimen can be of optimum thickness, when relatively large numbers of characteristic excitations occur but few electrons suffer multiple scattering. The relative number of first and second plasmons excited can be used to indicate the optimum specimen thickness.

Unfortunately the quantitative analysis of EEL spectra did not prove very useful during this project. The atoms to be detected were zirconium, copper and oxygen. The following problems were encountered:

(i) For zirconium only the $\text{Zr}_{M4,5}$ edge fell within the energy range of the spectrometer. No satisfactory theory has yet been developed to calculate values of $\sigma$ for edges other than $K$ and $L$.

(ii) The $\text{Cu}_L$ edge occurs at quite a high energy in the range of the spectrometer and the cross section for $\text{Cu}_L$ ionisations is low. Therefore the number of counts collected under this edge was low. As a result quantification was statistically inaccurate.

(iii) The specimens were seldom very thin so the number of multiply scattered electrons was significant. This meant that even the $O_K$ edge, which was otherwise favoured for quantification, proved to be a problem.
Rutherford Backscattering Spectroscopy (RBS).

RBS gains its name from the perpetrator of investigations into the Coulombic force between atoms. Rutherford used energetic \(\alpha\)-particles to study the distance from a gold nucleus beyond which the Coulomb interaction ceased to be effective. RBS is an analytical technique which uses He\(^+\) ions and gives surface and near-surface information about a sample. In this project it was used to study the near-surface composition of amorphous CuZr TEM specimens before and after ion implantation. The studies consisted of directing a 1.5MeV beam of He\(^+\) ions into the samples at normal incidence. The energy of the recoiling He\(^+\) particles was monitored at a take-off angle of 20°. Fig.6.6 is a schematic representation of the RBS apparatus.

The schematic representation of the spectrum that would be expected from a perfectly homogeneous specimen of CuZr is contained in fig.6.7. The horizontal axis is labelled in channel numbers. The higher the energy of the recoiling particle the higher the channel in which it is recorded. Two important pieces of information can be gained from RBS data, the mass of atoms within the specimen and the depth distribution of those atoms. In fig.6.7 it can be seen that the copper profile is superimposed on that of zirconium. Also copper is first recorded in lower channels, because it is the least massive atom. Any oxygen counts will be swamped at the low energy end of the spectrum by recoils from copper and zirconium deep in the specimen. These statements will be better understood if we consider the way in which the energy of a recoiling He\(^+\) ion is determined by the mass and depth of a target atom [Chu et al '78, Foti et al '77].
Fig. 6.6. A schematic diagram of the RBS apparatus.

Fig. 6.8. Energy loss in a thin specimen.
Fig. 6.7. A schematic RBS spectrum which might be expected from an ideal, homogeneous sample of amorphous CuZr.
(a) Mass Perception.

Energy is transferred from the incident ion to the target atom through a virtually elastic two-body collision. To describe the energy transfer the concept of a "kinematical factor" \((k)\) is used. The recoil energy \((E_1)\) can be obtained from the incident energy using;

\[
E_1 = KE_o
\]

where;

\[
k = \frac{[1 - (m_1/m_2)^2 \sin^2 \theta]^{1/2} + (m_1/m_2) \cos \theta]^2}{1 + (m_1/m_2)}
\]

The parameters in this equation can be seen in fig.6.6. Using equation 6.9 \(m_2\) can be calculated if \(m_1\) and \(\theta\) are known.

(b) Depth Perception.

From the moment an ion enters a solid its energy begins to be reduced. For a thin target the energy loss per unit distance travelled can be measured. This value is usually referred to as the "energy loss" at the incident energy. This statement really only applies in the limit as sample thickness tends to zero, as energy loss is a function of energy. Fig.6.8 shows the situation for a thin specimen, which leads to the equation;

\[
\lim_{\Delta x \to 0} \frac{\Delta E}{\Delta x} = \frac{dE(E_o)}{dx}
\]

Typically for beam energies between 0.5 and 3MeV He\(^+\) ions have energy losses of \(dE/dx=10\) to 100eV\(\cdot\)A\(^{-1}\). The next equation follows from this definition of energy loss;

\[
E_R = E_o - \int_0^x \frac{dE_o}{dx} \cdot dx + \int_x^0 \frac{dE_1}{dx} \cdot dn
\]

It shows that the measured recoil energy is sensitive to the depth at which the ion-atom collision took place. The two integrals account for energy
lost on the way in and out of the sample. On the way in the initial energy is $E_0$ while on the way out it is $E_1$.

It is possible to measure the relative amounts of copper and zirconium present because the recoil yield of a particular element is proportional to the square of its atomic number. The ratio of the number of copper to zirconium atoms can be determined from the simple relation;

$$\frac{N_{Cu}}{N_{Zr}} = \left(\frac{h_{Cu}}{h_{Zr}}\right) \cdot \left(\frac{Z_{Zr}}{Z_{Cu}}\right)^2 \quad \ldots \ldots 6.13$$

where $N_{Cu}$ and $N_{Zr}$ are the number of copper and zirconium atoms respectively and $h_1$ and $h_2$ are the heights of the two profiles, as shown in fig.6.7. The Z's represent the atomic numbers of the appropriate elements.

6.8 Energy Dispersive X-Ray Analysis.

The passage of electrons through a TEM specimen leads to the ionisation of some component atoms. This has already been discussed in terms of electron energy loss, where the energy spectrum of transmitted electrons is monitored. Ionisations of inner electron shells are frequently followed by electrons falling into the vacated shell from less tightly bound states. As a result characteristic X-rays are emitted. Elemental microanalysis can thus be performed in the TEM with the aid of an energy dispersive X-ray (EDX) spectrometer. EDX analysis took place in a Philips 400T electron microscope fitted with an X-ray detector and pulse processor supplied by "LINK Systems". An example of an EDX spectrum is contained in fig.6.9. It was collected from a gold film resting on a copper grid. Features of the spectrum are:
Fig. 6.9. An EDX spectrum from a gold specimen, confirming the absence of oxygen at the windowless detector.
(i) peaks corresponding to Cu\textsubscript{K}, Cu\textsubscript{L} and Au\textsubscript{M} X-rays.

(ii) the peaks are roughly Gaussian despite the fact that the X-rays ought to be monoenergetic. This fact arises primarily because statistical fluctuations occur in the number of electron-hole pairs created when each X-ray enters the solid state Si(Li) detector [Knoll '79].

(iii) Bremsstrahlung radiation provides the background counts upon which the characteristic peaks are found. The background is subtracted when quantitative analysis is performed.

(a) Quantitative Analysis.

The basic equation for EDX quantification was proposed by Cliff and Lorimer, it has the well known form;

\[
\frac{C_a}{C_b} = K_{ab} \cdot \frac{I_a}{I_b} \quad \ldots \ldots 6.14
\]

In this relation the ratio by weight of constituents a and b is given in terms of the ratio of their characteristic peak intensities above background, and the Cliff-Lorimer factor (\(K_{ab}\)). A measure of the confidence that can be attributed to this technique has been described by Statham ['82]. \(K_{ab}\) is obtained experimentally or theoretically for a particular pair of elements [Wood et al '84]. The value is independent of specimen thickness and composition, but does vary for different instruments and accelerating potentials. For a binary system the composition in weight percent can be calculated with the additional knowledge that;

\[
C_a + C_b = 100 \text{ wt}\% \quad \ldots \ldots 6.15
\]

The treatment can be extended to other systems using the relation;
\[ K_{ca} = K_{cb}/K_{ab} \quad \ldots 6.16 \]

This also allows ternary and higher systems to be dealt with, following the repeated use of equation 6.14. Values of \( K_{ab} \) can be obtained by three methods:

(i) From previously determined values using equation 6.16 above.

(ii) Experimentally, from compounds of known stoichiometry, using equation 6.14.

(iii) From first principles using the equation:

\[
K_{ab} = \frac{(Qwa/A)_b}{(Qwa/A)_a} \cdot \frac{\varepsilon_b}{\varepsilon_a} \quad \ldots 6.17
\]

where \( Q \) is the ionisation cross section and \( w \) is the fluorescence yield of the appropriate X-ray. \( a \) is the ratio of the intensities of the \( \alpha \) to the \( \alpha + \beta \) components of the spectrum and \( A \) is the atomic weight. The ratio \( \varepsilon_b/\varepsilon_a \) corrects for low energy X-rays being absorbed more than high energy ones as they enter the detector. Absorption occurs because the detector is protected by a beryllium window, it is coated with a gold contact layer and has a dead layer at its surface. The error in the value of \( Q \) can be great (~15%) which means that calculating \( K_{ab} \) by this method does not necessarily provide accurate results. There is also often great uncertainty in the knowledge of the beryllium window thickness.

Fig.6.10 shows how \( K_{ab} \) varies with characteristic X-ray energy. The curve climbs steeply at the low energy end, where the corrections needed to take account of photon absorption are high.

If it can be assumed that the specimen is sufficiently thin, very little X-ray absorption will take place in the specimen itself. The "thin
Fig. 6.10. The variation of $K_{A_{Fe}}$ for K X-rays with energy and hence atomic number.
film" criterion is said to be fulfilled and equation 6.17 can be applied. However, when absorption in the specimen becomes significant (as is nearly always the case for low energy X-rays) a further correction must be used [Williams and Goldstein '81]. The value of $K_{ab}$ is adjusted using the equation:

$$K^*_{ab} = K_{ab} \frac{\int_0^t \phi_b \exp\left\{-\frac{(\mu/\rho)_b}{\phi} \cdot \csc \alpha \cdot (\rho t)\right\} dt}{\int_0^t \phi_a \exp\left\{-\frac{(\mu/\rho)_a}{\phi} \cdot \csc \alpha \cdot (\rho t)\right\} dt}. \tag{6.18}$$

The terms $\phi_a, b$ describe the depth distribution of the elements through the specimen. $\phi$ and $t$ are the specimen density and thickness, $(\mu/\rho)_a, b$ are the mass absorption coefficients for the generated X-rays in the specimen and $\alpha$ is the X-ray take-off angle. It is almost always assumed that $\phi_a = \phi_b = 1$, i.e. that the elements are homogeneously dispersed through the thickness of the sample. Indeed the available commercial software for EDX quantification deals only with this assumption. This is basically because depth distributions are very seldom known. In the case of ion implantation some idea of the depth distribution of the implanted species can be obtained. This knowledge will be used later in this thesis to modify the conventional equation for absorption correction which is shown below:

$$K^*_{ab} = K_{ab} \frac{(\mu/\rho)_a}{(\mu/\rho)_b} \left[1 - \exp\left\{-\frac{(\mu/\rho)_b}{\phi} \csc \alpha \cdot (\rho t)\right\}\right] \tag{6.19}$$

(b) Light Elements.

As already mentioned the amount of X-ray absorption increases as the photon energy decreases. For atoms smaller than fluorine absorption in the detector window is so great that their X-rays cannot be detected at all. In certain cases, where a high vacuum is achieved in the TEM, it is possible to remove the detector window and so detect oxygen, nitrogen, carbon and even boron. It has been noted that removal of the window can
lead to water vapour condensing on the Si(Li) crystal. This leads in turn to spurious oxygen counts being registered as a result of X-ray fluorescence. This effect would have been particularly detrimental in this project as the presence of oxygen is of interest. To ensure that no ice was present at the detector a gold film was analysed. The resulting spectrum is displayed in fig.6.9. The Bremsstrahlung background is high at the low energy end of the spectrum because the window had been removed, but no significant peak can be seen at the position that would correspond to $O_K$ X-rays. As a result of this analysis oxygen detected during this project could only be attributed to CuZr specimens.
7 Results.

7.1 The Metallic Glass.

7.1.1 The Amorphous CuZr Ribbon.

Initial observations of the metallic glass were performed in an SEM, immediately after melt-spinning. Micrographs of the ribbon surface are contained in fig.7.1a and fig.7.1b and both show signs of significant texture. The air-side is seen to be covered in "V-shaped" ridges which point along the length of the ribbon. These features probably formed as a result of directional solidification below an oxide layer. The oxide layer would have solidified before the underlying metal. As the metal solidified during its journey on the copper substrate, its volume would have decreased, causing the oxide to deform. On the wheel-side large troughs (up to 5um across) run along the length of the ribbon. These would have formed when air was trapped between the melt puddle and the copper substrate.

To examine the thickness of the surface layer, which was suggested by the V-shaped ridges on the air-side, some samples were mounted in cross section and examined in the SEM. An example of the micrographs obtained is shown in fig.7.2. A region of different contrast was observed at the air-side, as indicated by the arrows in fig.7.2. No
Fig. 7.1. SEM images of ribbon immediately after spinning: a). the "air-side", b). the "wheel-side".
Fig. 7.2. Two adjacent ribbon cross-sections. Arrows indicate the air-side and its surface layer.
such contrast change was noted at the wheel-side. This surface layer was analysed in the SEM with the aid of an EDX detector. Table 7.1 holds the results of this brief investigation. Copper, zirconium and oxygen could be detected in all the regions analysed. However, more zirconium and oxygen was detected in the layer region than in the rest of the specimen. From these results we can only deduce that more oxygen was present in the air-side layer than in the underlying material, more quantitative weight cannot be attributed to this data because the quantitation routine for data collected in the SEM assumes a homogeneous distribution of elements. In this case, as in the case of TEM specimens which will be dealt with later, the EDX evidence alone cannot tell us whether oxygen is homogeneously present in the region analysed or not. The extra zirconium present in the layer region probably reached it as a result of preferential oxidation during solidification.

Apart from the surface layer the only other major inhomogeneities observed in the cross sectioned specimens were pores. No evidence of crystallinity was observed in the specimen. Confirmation of the amorphous nature of the samples was obtained with an X-ray diffractometer. An example of the trace from an "as-spun" specimen is shown in fig. 7.3. The width of the first diffuse peak suggests that no order existed in the structure above a scale of ~10nm [Warren '69]. The trace does show a small well defined peak which corresponds to monoclinic zirconia. This peak was lost if the specimens were mechanically polished, so the zirconia was to be found at the surface. Similar observations were made by Calvayrac et al ['80].

To ensure that the amount of oxygen dispersed through the samples was as small as possible DSC was performed on each sample produced. The
Fig. 7.3. An X-ray diffraction pattern obtained from the amorphous CuZr alloy used during this project. The pattern features two diffuse peaks which correspond to the first and second coordination distances of atoms in the amorphous alloy (a-CuZr), and the (111) reflection from monoclinic zirconia (m-ZrO$_2$).
Table 7.1.

Alloy Content in Weight Percent.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Zr</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>40</td>
<td>58</td>
<td>2</td>
</tr>
<tr>
<td>Layer</td>
<td>31</td>
<td>64</td>
<td>5</td>
</tr>
</tbody>
</table>

These results were obtained by analysing five specimens in the SEM. The standard deviation on each value was the order of 1wt%.
traces produced were compared with those reported by Polk et al ['78], who studied the effect of adding small amounts of oxygen to amorphous CuZr. A typical trace for the material used during this project is contained in fig.7.4. It can be seen that the trace compares well with that for ribbon which contained no oxygen in fig.2.16.

Some of the metallic glass was annealed for three hours at 600°C in an ultra-high vacuum furnace. The samples became brittle and crystallisation had clearly occurred. X-ray diffraction was used to identify the products of crystallisation. The resulting trace is contained in fig.7.5. The majority of lines produced could be attributed to the equilibrium phase Cu$_{10}$Zr$_7$. The presence of monoclinic zirconia was also evident. As described in section 2.5.2 this result was expected for the bulk alloy under good vacuum conditions and for a long anneal.

7.1.2 A TEM Study of the Amorphous CuZr Alloy.

Observation of the microstructure of implanted amorphous CuZr using the TEM forms an important part of this thesis. This section presents the results of TEM observations made before ion implantation. Fig.7.6 shows a TEM image obtained from a thin foil prepared by electropolishing. No evidence of crystallinity can be seen. The evident mottled contrast is a feature frequently noted in TEM studies of amorphous metals. It has been suggested that this contrast is an indication of local ordering, indeed the use of high resolution TEM to study local atomic order in amorphous materials has been attempted
Fig. 7.4. The heat flow profile obtained from the amorphous CuZr alloy by differential scanning calorimetry.
Fig. 7.5. An X-ray diffraction pattern obtained from the melt-spun CuZr ribbon. The indexed lines correspond to reflections from Cu$_{10}$Zr$_7$. 
Fig. 7.6. a). TEM bright field image of the amorphous alloy, b). the diffraction pattern from this region.
Efforts have met with little success and have largely ceased because the interpretation of high resolution images requires the generation of computed images. This requires some a priori knowledge of atomic arrangements. A major problem for high resolution TEM is to insure that specimens are extremely thin and have a smooth surface. For metallic glasses these criteria are difficult to fulfil. It is possible that the mottled contrast is entirely due to slight variations in specimen thickness.

Fig. 7.6b is a diffraction pattern taken from the area shown in fig. 7.6a. Diffraction patterns were obtained from several areas and the diffuse haloes were found to be centered on the following interatomic spacings: first coordination distance ~0.22nm, second coordination distance ~0.355nm. These results are in good agreement with the X-ray diffraction trace in fig. 7.3. There is also good agreement between these results and data obtained by Scott ['77] for a Cu_{60}Zr_{40} alloy.

7.1.3 Oxygen in the Thin Foil Specimens.

It is not surprising that oxygen is often present in TEM specimens prepared by electropolishing techniques, as oxidation is a necessary part of the thinning process. In the case of CuZr this is particularly true because zirconium and its alloys are known to have a high affinity for oxygen. However oxygen could enter the specimen at any one of the following stages:
(i) Alloy production in the argon arc furnace.
(ii) When the alloy was molten prior to melt-spinning.
(iii) When the ribbon was cooling after melt-spinning.
(iv) During sample storage (specimens were kept in a vacuum desiccator).
(v) When the material was electropolished for the TEM.

Items (i) and (ii) in the above list may have led to small amounts of oxygen being introduced throughout the alloy. Item (iii) is only likely to have led to the formation of the oxygen containing layer discovered on the air-side. This was of course removed by mechanical polishing before electropolishing was performed. Items (iv) and (v) would probably have led to the near surface presence of oxygen.

To investigate the amorphous specimens before implantation analytical techniques were employed and two simple models were proposed to represent the TEM specimens. These models are best described with the aid of the diagrams in fig.7.7. "Model a" was a wedge shaped section of pure CuZr with a thin, oxygen containing surface layer. "Model b" was a wedge in which copper, zirconium and oxygen were homogeneously dispersed. It was important to discover which model most nearly represented the TEM specimens because the presence of oxygen is known to affect the behaviour of inert gas atoms in metals. The following sub-sections, which are labelled a to d, describe the use of a variety of techniques to indicate the way in which oxygen was distributed through the specimens.
Fig. 7.7. Two models to represent the specimens produced by electrochemical thinning.
(a) **Electron Diffraction.**

Initial studies suggested that the diffraction patterns only contained features that could be attributed to the amorphous alloy. However, careful study of the patterns using an on-line computer system revealed that a shoulder was in fact present on the inside of the first diffuse halo. Fig. 7.8b shows one such trace which came from a region of the sample estimated to be ~150nm thick. Moving to a thinner (~100nm thick) region of the specimen fig. 7.8a was collected. This shows that the first halo had split into two diffuse rings. The outer ring is in a position that corresponds to the first coordination separation of the metallic glass, while the inner one falls in the same position as the shoulder in fig. 7.8b. This peak lies close to the d-spacing of the (111) reflection from monoclinic zirconia. The width of both rings suggests amorphous or extremely microcrystalline material. As the area selected for the diffraction pattern approached the edge of the thin foil the intensity of the inner halo increased in relation to the outer one. These observations provided circumstantial evidence for model a, because the surface oxygen-containing layer would only be expected to make a significant contribution to the scattering of electrons in the thinnest parts of the specimen. In thicker regions the contribution from the CuZr would be far greater. The innermost ring was not detected initially because there is a natural tendency to set exposure times to the brightest part of the diffraction pattern.

(b) **Electron Energy Loss (EELS).**

The technique of EELS was described in section 6.6, with particular reference to the measurement of specimen thickness in the TEM. A
Fig. 7.8. Electron diffraction intensity from; a) a thin region and b) a thick region of an amorphous TEM specimen of CuZr.
plasmon mean free path was calculated with the aid of contamination spot measurements (as shown in fig.6.5) and with equation 6.4. The series of thickness measurements used to derive a value of \( L_p \) are contained in table 7.2. They indicate that the mean free path for plasmon excitations due to 100keV electrons in amorphous CuZr is 136±14nm. This measurement has been used repeatedly throughout the rest of this results section when thicknesses are quoted. Although the accuracy of this technique is not expected to be high it provides a rapid way of gauging specimen thickness for both unimplanted and implanted specimens.

EELS was also used to investigate the composition of specimens but quantification was only possible for a few specimens (see section 6.6). However, spectra such as that in fig.7.9 did allow the ratio of oxygen to copper counts to be calculated and plotted as a function of specimen thickness. Fig.7.10 shows that the ratio \( N_O/N_{Cu} \) increased with decreasing thickness. This lent support to model a but was not considered strong evidence because the effects of multiple scattering were significant and the low number of copper counts collected meant the data had a standard deviation in excess of 10%.

(c) Rutherford Backscattering Spectroscopy (RBS).

As mentioned in section 6.7 RBS is not capable of detecting oxygen atoms amongst the copper and zirconium. Despite this, interesting near-surface effects were detected using this technique. The type of spectrum that would be expected if copper and zirconium were homogeneously dispersed through the specimen was discussed in section 6.7 and it was shown that the ratio of copper to zirconium atoms could be deduced using equation 6.13. Fig.7.11 shows an actual spectrum
Fig. 7.9. An EEL spectrum obtained from amorphous CuZr. Two gain changes are required for the low-loss region to be displayed with the Zr, C, O and Cu edges.
Fig. 7.10. EELS data indicating that an oxygen containing layer existed at the specimen surface.
Fig. 7.11. A Rutherford backscattering spectrum obtained from an unimplanted TEM specimen of amorphous CuZr.
<table>
<thead>
<tr>
<th>Spec. thickness (nm)</th>
<th>643</th>
<th>505</th>
<th>605</th>
<th>748</th>
<th>707</th>
<th>578</th>
<th>580</th>
<th>500</th>
<th>590</th>
</tr>
</thead>
<tbody>
<tr>
<td>λp (nm)</td>
<td>1436</td>
<td>1128</td>
<td>1189</td>
<td>1470</td>
<td>1388</td>
<td>1381</td>
<td>1491</td>
<td>1290</td>
<td>1509</td>
</tr>
</tbody>
</table>
collected from an unimplanted amorphous sample of electropolished CuZr. A slight peak is seen to occur at the near-surface (high energy) end of the copper profile. By comparison with a theoretical prediction of the shape that the zirconium ought to have at the surface it was possible to see that the specimen was significantly depleted in zirconium in this region. From the relative heights of the near-surface profiles the specimen was found to have an average composition of Cu$_2$Zr near its surface. Each channel of the spectrum was found to correspond to a depth increment of 3nm. This led to the conclusion that the near surface layer extended over a distance of ~24nm. Further, Dr. C. Jeynes of the University of Surrey was able to estimate the relative amount of oxygen contained in this layer by calculating the total number of recoils that would have been expected for different oxygen contents. The layer was found to have an average composition of ~Cu$_2$ZrO$_2$.

It is clear from this result that TEM specimens prepared by electropolishing had a copper-rich layer at their surfaces which contained some oxygen. However, the RBS technique was not considered a reliable source of information as far as the content of oxygen was concerned. To strengthen the conclusion that oxygen was present throughout the near-surface layer windowless EDX was applied in the TEM.
As described in section 6.8, conventional quantitation of EDX data requires the assumption that all elements are homogeneously dispersed within the specimen. This is clearly not the case for the specimens used during this project. We can further confirm this fact by comparing a plot of $O_K$ counts against thickness with the trends that might be expected for models a and b. Fig. 7.12 represents the data trends. Model a would result in a generally decreasing set of data points with increasing thickness, as the bottom surface of the foil would be subject to increasing X-ray absorption as it got further from the top surface. A constant level would be reached when the bottom surface ceased to contribute to the $O_K$ X-ray signal. For model b, the intensity of $O_K$ X-rays would increase until the specimen became thicker than the depth from which $O_K$ X-rays could escape. Fig. 7.13 contains experimental data taken from an electropolished sample of amorphous CuZr. The horizontal axis provides the specimen thickness which was obtained from EELS data. A clearly decreasing trend is seen indicating that the oxygen is limited to a surface layer.

So far no technique has been described which could indicate the depth to which oxygen was present. To pursue this problem using EDX spectroscopy it was necessary to assume that the composition of the surface layer was $Cu_2ZrO_2$, as suggested by RBS. A computer routine was then written to generate plots of the ratio of intensities of the oxygen and copper peaks ($I_O/I_{Cu}$) as a function of specimen thickness, for various thicknesses of the surface layer. The equation required for such calculations was based on equation 6.18, which is used to correct for X-ray absorption within the specimen and
Fig. 7.12. The expected trends for $O_K$ intensity with increasing specimen thickness.
Fig. 7.13. EDX spectrum obtained with a windowless detector from electrochemically thinned CuZr.
Fig. 7.13a. Oxygen counts as a function of the thickness of an electrochemically thinned sample of CuZr. The square root of the number of counts indicates the possible vertical error ($\sigma \approx 3\%$). Horizontally errors of $\approx 10\%$ are expected to arise from the EELS thickness measurement.
equation 6.14. The resulting relationship was:

$$\frac{I_{0K}}{I_{CuK}} = K_{Cu} \frac{C_{0}}{C_{Cu}} \frac{\left\{1 - \exp\left[-(u/p)_{L}^{0}\rho_{L}t_{L}\csc\alpha\right]\right\}}{\left\{1 - \exp\left[-(u/p)_{CuZr}^{0}\rho_{CuZr}(t - 2t_{L})\csc\alpha\right]\right\}} \times \frac{\left\{1 + \exp\left[-(u/p)_{CuZr}^{0}\rho_{CuZr}(t - t_{L})\right]\right\}}{\left\{1 + \exp\left[-(u/p)_{L}\rho_{L}t_{L}\csc\alpha\right]\right\} / (u/p)_{CuZr}^{0}}$$

which includes the parameters:

- $C_{0}$ average weight percent of $O$ in the layer.
- $C_{Cu}$ average weight percent of $Cu$ in the specimen.
- $(u/\rho)_{L}^{0},(u/\rho)_{CuZr}^{0}$ mass absorption coefficients of $O_{K}$ in layer and bulk.
- $(u/\rho)_{L}^{Cu},(u/\rho)_{CuZr}^{Cu}$ mass absorption coefficients of $Cu_{K}$ in layer and bulk.
- $\rho_{L},\rho_{CuZr}$ densities for layer and bulk.
- $t, t_{L}$ specimen thickness and layer thickness.
- $\alpha$ take-off angle for X-rays.

The theoretically calculated results were then compared with the experimental data, as shown in fig.7.14. A theoretical curve generated on the assumption that oxygen was homogeneously distributed through the foil is also plotted in this figure. Inspection shows that the data are best fitted by assuming the oxygen-containing layer to be 22.5nm thick. This is in good agreement with the thickness of the surface layer of 24nm detected by RBS. This means that the oxygen penetration had occurred to a depth similar to that of the copper rich layer.

In this section it has been confirmed that electropolishing results in the preferential removal of zirconium from the specimen surface. It has also been shown that considerable quantities of oxygen entered the specimen during the process.
Approximating the Depth of Oxygen Penetration.

N.B. Assumed Stoichiometry of Oxide Layer: Cu₂Zr₁O₂.

Fig. 7. Determining the depth to which oxygen was present in an electrochemically thinned specimen of CuZr.
7.1.4 Phenomena Induced by the Electron Beam.

It has already been mentioned, in chapter 5 on radiation damage, that electrons of sufficient energy can cause atomic displacements in a metal specimen during electron microscopy. Although most electrons pass through a TEM specimen without losing a large amount of energy, significant beam heating can occur. This is particularly worth noting when the beam is to be highly focussed. As described in section 5.6 high voltage microscopes have caused crystallisation to occur in some amorphous metals, and amorphisation to occur in some crystalline ones. Any effects induced by the electron beam are important in the context of this project because they occur through radiation damage. The resistance to this damage exhibited by amorphous CuZr is in itself interesting, and had to be minimised during microanalytical studies.

A qualitative assessment of the effect of the electron beam was performed by subjecting a specimen to a highly condensed beam of 120keV electrons. The experiment was performed in a Philips EM400T at "spot size 2". These conditions provided a beam current several times greater than that used for EDX or EELS analysis.

Windowless EDX indicated that the oxygen content of the damaged region increased at a rate of ~3atOMIC% per minute (this was using the conventional quantitation system). After three minutes the region was seen to contain small crystallites; the effect is shown in fig.7.15. Fig.7.16a and b contain diffraction patterns collected from this region before and after the specimen was damaged. The formation of crystallites suggests that the specimen had locally reached temperatures
Fig. 7.15. Crystallites induced by the intense electron beam.
Fig. 7.16. Diffraction patterns taken from the area in fig. 7.15: a) before and b) after the beam was condensed.
of the order of 700K. It seems probable that the uptake of oxygen occurred as a result of this increase in temperature. It is possible that both crystallisation and oxygen uptake were aided by radiation enhanced diffusion, rather than by an increase in temperature alone.

The flux of electrons in the beam was estimated to be $\sim 10^{18} \text{ecm}^{-2}s^{-1}$ during the experiment. Typical fluxes during EDX or EELS analysis were estimated to be $\sim 10^{17} \text{ecm}^{-2}s^{-1}$. No microstructural changes were observed after spectra were collected.

It appears that the beam damage suffered during analysis was insignificant, as the typical collection time of 100s led to $\sim 10^{19} \text{ecm}^{-2}$ hitting the specimen while $\sim 2 \times 10^{20} \text{ecm}^{-2}$ were required to cause observable damage during the high beam current experiment described above.
7.2 Inert Gas Ion Implantation.

7.2.1 Ion Beam Milling.

Ion beam milling is a technique often used as the final preparatory stage for TEM specimens. The results described in this section pertain to the application of this technique to amorphous CuZr. The technique basically involves directing low energy (~5keV) inert gas ions at both sides of the specimen. It is usually assumed that atoms are removed from the specimen surface but few inert gas ions are implanted. Under most circumstances this is a reasonable assumption because ions impinge on the specimen at glancing angles (up to 80° to the perpendicular). For these conditions argon ions have a range of only 1.2nm in CuZr. It is also usually assumed that milling does not induce microstructural changes. In fact ion milling does result in the formation of small defects, as reported by Cullis ['78]. Indeed low energy ion guns designed for ion milling have been used for inert gas implantations [Van Swijgenhoven et al '84].

In this project the following final conditions for thinning amorphous CuZr with argon ions were investigated: voltage, 5keV, current, 0.2mA, angle of impingement, 75°. The current indicates an approximate dose rate of \( \sim 3 \times 10^{14} \text{Ar}^+ \text{cm}^{-2} \text{s}^{-1} \).

At low magnifications in the TEM the specimens appeared to be free of defects. However, windowless EDX analysis revealed the presence of
oxygen and argon. Fig.7.17 shows the EDX spectrum collected from this area. The spectrum contains argon peaks of significant size. As a result of this observation it was decided that ion beam milling should not be used to prepare specimens for higher energy argon implants, as the argon content would be affected by the preparation technique. When the magnification was increased small bubbles became evident, as fig.7.18 reveals. The TEM conditions for imaging small cavities have been discussed by Ruhle and Wilkens ['75], Stobbs and Gibson ['77] and Van Landuyt et al ['65]. No crystallisation was observed. The distribution of bubble sizes is quite narrow in this image, with the mean radius being approximately 1nm. According to Bangert et al ['86] no previous examination of TEM specimens has revealed the presence of distinct gas bubbles at such a high angle of ion impingement. It is surprising that bubbles were observed as the range of the ions was calculated to be 1.2±1.0nm. Bubbles of this size are expected to be relatively mobile according to the equations described in section 3.5.2, so several specimens were annealed in the TEM with the aim of observing migration and coalescence in the amorphous metal. However, no bubble movement was observed over periods of hours below the crystallisation temperature of 750K. Indeed even when atomic mobility was sufficient for crystallisation to occur the cavities remained stable. Fig.7.19 contains a series of micrographs taken during annealing and crystallisation. Diffusion of metal atoms did cause some cavities to break the surface.

Bangert et al ['86] performed a series of similar experiments on ion beam thinned silicon. They observed that during annealing argon was lost from the specimens but the cavities remained stable. They concluded that argon left the specimens through atomic level diffusion
Fig. 7.17. EDX spectrum obtained with a windowless detector from ion beam milled amorphous CuZr.
Fig. 7.18. Images of bubbles in ion milled amorphous CuZr: a). underfocus, b). overfocus.
Fig. 7.19. Micrographs of the ion milled specimen taken during annealing at 600K for: a) 5, b) 20 and c) 100 minutes.
and that the stability of the cavities was the result of oxygen being knocked in from the surface. It seems likely that the situation was similar in the case of CuZr, with the cavities being stable because they lie within an oxygen-containing layer.

To confirm the existence of an oxygen-containing layer EDX data was collected from several areas on one specimen so that the ratio of the intensities of the $O_K$ and $Cu_K$ peaks could be plotted as a function of specimen thickness. It was assumed that the ion milled specimen was mostly CuZr with a surface layer of CuZrO$_2$. A fit to the experimental data was obtained using equation 7.1. The results are displayed in fig.7.20, and suggest that oxygen was present in the specimen to a depth of ~9nm.

How might oxygen find its way into an ion milled specimen? Certainly a layer of oxide would have been present on the specimen prior to milling, but the final content is unlikely to be related to the original situation because microns of material were remove during the thinning process. The following mechanisms could have accounted for the formation of an oxygen containing layer, in dynamic equilibrium, during milling:

(i) The knock-in of oxygen atoms from the specimen surface by incoming argon ions. This mechanism has been used by Cox et al ['84] to account for the presence of oxygen at the surface of bubbles in aluminium, and by Bangert et al ['86] and Evans ['87] to explain the high stability of cavities in silicon. Let us consider the range of recoiling oxygen atoms. The maximum energy
Fig. 7.20. Determining the depth to which oxygen was present in an ion milled specimen of amorphous CuZr.
transferred in a collision between a 5keV argon ion and a stationary oxygen atom is \( E_m = 2.05 \text{keV} \). The range for such recoiling atoms in CuZr, at an angle of 75°, is 1.5±1nm. The maximum distance to which oxygen atoms could have been knocked into the specimen was ~3.5nm.

(ii) Oxygen atoms could have diffused into the specimen, perhaps more quickly than under normal conditions of temperature and pressure. Ion beam milling is known to increase the temperature of the sample, while the low partial pressure of oxygen required for the process could prevent the formation of a passivating oxide.

It seems likely that oxygen uptake during ion bombardment is the result of a combination of the processes described above. A similar observation was made by Parsons et al who noted the formation of ZrO\(_2\) on zirconium during neon implantations [Parsons et al '81]. They recalled that energy loss took place through atomic displacements and interactions with electrons, which leads to an increase in temperature, so that the effect was attributed to knocked in atoms and enhanced diffusion.

In order to obtain some idea of the extent to which the milling process increased atomic mobility in the surface of the metallic glass equation 3.4 was used. This expression was developed by Greenwood et al to calculate the separation of inert gas bubble nuclei. This means that it can only be applied to the early stages of bubble growth, before coalescences affect the population. It seems reasonable to apply the equation to the bubbles observed during this study because the milling process removes material at a rate of several Angstroms per second,
while the bubbles could be no deeper than a few nanometers. The following values were used in equation 3.4 to calculate the gas diffusion coefficient, with the estimation of gas arrival rate requiring the assumption that the gas came to rest within 3nm of the surface:

Gas arrival rate per atom site, \( G = 0.0184 \text{Ar} \text{at}^{-1} \text{s}^{-1} \).

Half the bubble separation, \( r_1 = 3 \text{nm} \).

Bubble radius, \( r_b = 1 \text{nm} \).

Mean atomic dimension, \( a = 0.3 \text{nm} \).

These values indicate that the gas diffusion coefficient during implantation was \( D = 4 \times 10^{-12} \text{cm}^2 \text{s}^{-1} \). This result is comparable with coefficients evaluated by Lane and Goodhew ['84], for grain boundary diffusion in an austenitic alloy at 600°C. It is also comparable to values for helium diffusion in gold, silver and aluminium at 800°C, as reported by Sciani and Jung ['83]. The bubble population found in the ion beam thinned specimens is therefore consistent with relatively high inert gas atom mobility, similar to that found when crystalline metals are heated to \( 0.5T_m \) or more. The crystallisation temperature \( T_x \) of amorphous CuZr is 750K, and it is thus surprising that the gas diffusion coefficient was high yet no crystallisation was observed. Radiation enhanced diffusion (RED) was probably responsible for the high diffusion coefficient derived above. This phenomenon occurs because incoming ions cause atomic displacements, i.e. Frenkel defects or for amorphous alloys quasi-vacancy/quasi-interstitial pairs. The fact that the enhanced atomic diffusion did not lead to crystallisation indicates that the specimen temperature did not approach \( T_x \) and that thermal energy associated with collision cascades was rapidly dispersed. These effects will be discussed further in chapter 8. The possible effects of RED have also been discussed by Dearnaley ['82] and Matzke ['82].
The stability of the amorphous phase in the implanted region may also have been enhanced by the introduction of oxygen. This factor will be discussed further in the next section, where the results of argon implantations at a higher energy are presented.

7.2.2 Argon Ion Implantation.

To further study the effect of high mass inert gas ion implantation on the metallic glass TEM specimens were prepared by electropolishing and subjected to bombardment by 80keV argon ions. In the previous section it was seen that low energy argon ions caused oxygen to enter the specimen surface and argon bubbles to form. The use of higher energy ions increases the depth to which argon is implanted and the number of displacements caused by each incident particle. Comparison between low and high energy implants thus allows the stability of the amorphous phase to be investigated under different damage distributions.

The experiments were performed at room temperature, with the ion beam meeting the specimen at 45°. The range for the ions was calculated to be $R_p = 31 \pm 18 \text{ nm}$. This meant that the majority of the gas came to rest at depths greater than the thickness of the oxygen containing layer detected in section 7.1.3 ($t_o = 24 \text{ nm}$). The dose rate was $7.94 \times 10^{13} \text{ Ar}^+ \text{cm}^{-2} \text{s}^{-1}$ and the doses used ranged from $4 \times 10^{16}$ to $3 \times 10^{17} \text{ Ar}^+ \text{cm}^{-2}$.

Observation of the implanted specimens revealed that large cavities were produced in most cases. Initially interest was focussed on the
nature of the implanted surface region. Electron diffraction indicated that no crystallisation had taken place. The analytical techniques of RBS and EDX analysis, which have already been discussed in chapter 6 were again employed.

7.2.3 The Near Surface Composition of Argon Ion Implanted Specimens.

(a) Rutherford Backscattering Spectroscopy.

The RBS spectrum obtained from a specimen which had been implanted to a dose of $2 \times 10^{17} \text{Ar}^+ \text{cm}^{-2}$ is displayed in fig.7.21. Comparison with fig.7.11, which contains the spectrum obtained from an unimplanted specimen, reveals an increase in the height and width of the hump at the near-surface end of the copper profile. Analysis of the spectrum indicated that the surface regions of the specimen had been significantly modified by implantation. A layer with an average metal atom concentration ratio of $\text{Cu}_{2}Zr$ was found to be present. The thickness of this layer was 69nm. It is interesting to note that the maximum range of the implanted ions, given approximately by $R_p + 2\sigma_{R_p}$, was ~67nm. This clearly suggests that the modification is related to the penetration depth of incoming ions. The nature of the modified surface layer was further investigated using EDX analysis.
Fig. 7.21. A Rutherford backscattering spectrum from a TEM specimen implanted with argon ions to a dose of 1.5x10^{17} \text{Ar}^+ \text{cm}^{-2}. 
Once again the depth to which oxygen had penetrated the specimen was estimated using equation 7.1. The theoretical values of $O_{K}/Cu_{K}$ as a function of specimen thickness were calculated on the basis of a surface layer of composition $Cu_{3}ZrO_{2}$. Fig.7.22 contains the experimental data and three theoretical curves for different thicknesses of oxygen-containing layer. It can be seen that the penetration depth of oxygen was approximately 70nm. This result is in close agreement with the maximum range of argon ions during implantation.

Let us consider the possibility that the oxygen entered the specimen because of atomic displacements. The maximum energy that could be transferred to an oxygen atom from an 80keV argon ion is $E_{m}=65.6$keV. On average therefore a recoiling oxygen atom would be given $\approx 32.8$keV. At $45^\circ$ to the perpendicular the projected range for such recoiling atoms would be 22±14nm. So the maximum depth to which oxygen may have been knocked into the specimen was $\approx 50$nm. This is quite close to the estimated depth of oxygen penetration. It is possible that diffusion may have helped oxygen to move further into the specimen, taking it to depths even closer to the estimated 70nm. However, the accuracy of the technique applied to obtain this value does not allow us to conclude whether diffusion and displacements were both required for the observed surface layer to form.

The copper enrichment provides an interesting problem. Calculations using the TRIM code were performed by Dr R. Webb of the University of Surrey, in an attempt to decide whether the enrichment could be accounted for by purely dynamical considerations. That is, if it were
Fig. 7.22. EDX spectrum from a sample of amorphous CuZr implanted to a dose of 2x10¹⁷ Ar⁺ cm⁻².
Fig. 7.22a. Determining the depth to which oxygen was present in argon implanted specimens of amorphous CuZr.
assumed that the copper and zirconium atoms were bound with equal strength at the surface, would the enrichment have occurred simply because one species was heavier than the other and thus received on average less energy. The TRIM code predicted that more copper atoms should have been sputtered than zirconium ones. The ratio was 1.13:1. This suggests that the surface layer should have been rich in zirconium after implantation. As this was not the case the following mechanisms for copper enrichment were considered:

(i) The binding energy for copper was significantly higher than that of zirconium in the amorphous alloy.

(ii) A thin layer of zirconia rapidly formed at the specimen surface. This was continuously removed as implantation took place. This layer meant that copper atoms were not encountered at the very surface of the specimen. Initially therefore the rate at which zirconium atoms were lost from the specimen was higher than that of copper atoms. After some time a state of equilibrium was reached in which both atoms were sputtered at equal rates because the implanted region (from which some atoms leave the specimen) was rich in copper.

In section 2.6 several references were made to layers of zirconia forming at the surface of amorphous CuZr. The surface layers of crystalline CuZr were found to contain no copper in one particular oxidation investigation, while copper rich crystals formed underneath. These observations lend support to the second possible mechanisms described above.
It is perhaps surprising that the amorphous metal retained this structure after ion bombardment to a relatively large dose. However, despite the significant amount of copper enrichment detected the composition of the implanted layer still lay in a region of the phase diagram where the amorphous phase is almost as thermodynamically stable as the equilibrium crystalline phase. Although ion implantation introduced considerable amounts of energy to the target material it also introduced atomic displacements. As long as the rate at which energy was dissipated from displacement cascades was sufficiently high and the specimen temperature did not approach $T_x$ the amorphous phase was sure to be retained. Fig. 2.13 is a phase diagram for the copper-zirconium system on which regions where the amorphous phase is thought to be stable with respect to the equilibrium phases have been marked. The figure includes a region where high glass forming ability has been verified by rapid quenching of the melt to produce the amorphous phase, and a region of high glass forming ability predicted by Saunders and Miodownik ['86]. It can be seen that the composition of the specimens investigated during this project fall within the regions where the amorphous phase is expected to be relatively stable. An alternative (or perhaps additional) source of phase stability is the introduction of oxygen to the system. It is impossible to decide which effect is dominant from the information gathered during this project. It would be interesting to prepare amorphous samples containing significantly more copper than zirconium and repeat the implantations. If implantation then induced copper enrichment the alloy composition would be shifted outside the range of good glass forming ability. The continued existence of an amorphous phase after such an experiment would indicate the importance of oxygen to the stability of this phase.
7.2.4 The Argon Content of Implanted Foils.

Cavities were seen to form in all foils irradiated to doses in excess of $5 \times 10^{16} \text{Ar}^+ \text{cm}^{-2}$. However, the gas content of the foil was unknown. EDX analysis was used to investigate the argon content of foils over a range of doses.

EDX spectra were obtained from several regions of each specimen. Conventional quantification of the spectra was performed with the aid of the on-line computer facility. The results are displayed in fig. 7.23, where the argon content is plotted as a function of implanted dose. The following trends can be observed:

(i) At low doses the argon content was roughly proportional to the implanted dose.

(ii) At no point on the curve does the experimental data fall on or above the dotted line that indicates $100\%$ argon retention. This was expected because during implantation some atoms are scattered backwards from the specimen surface. Others leave the specimen by diffusive processes or because the surface is eroded by the incoming ions.

(iii) Saturation in the measured argon content occurred between doses of $10^{17}$ and $1.5 \times 10^{17} \text{Ar}^+ \text{cm}^{-2}$. The ions involved in this implantation were relatively massive, saturation was thus expected to occur through surface erosion. A detailed description of this mode of saturation was presented in section 4.4.
Fig. 7.23. Argon content as a function of dose (conventional EDX quantification).
In section 4.4.2 it was noted that saturation is expected to occur when the surface has receded past the position of the initial maximum range of implantation ($R_p + 2\sigma_{R_p}$). A situation of dynamic equilibrium then exists between the rate of gas arrival and the rate of gas loss due to surface recession. The speed with which the surface recedes can be calculated if the time to saturation and $R_p$ are known. Additionally, with knowledge of the dose rate, the sputter coefficient can be calculated in atoms per ion ($S_{Cu/Zr}$).

Equation 7.1 was developed to estimate the depth of oxygen penetration from the ratio of oxygen to copper counts in EDX spectra. To perform these calculations approximate atomic concentrations had to be known. In this section the atomic percentage of argon to be found in the ion implanted surface layers of specimens will be calculated. This is possible as long as the projected ion range is known. The following equation was developed for this purpose, again from the theory of X-ray absorption;

$$C_{Ar} = \frac{1}{K_{CuA}} \frac{I_A (\mu/\rho)_A}{I_Cu (\mu/\rho)_Cu} \frac{1 - \exp[-(\mu/\rho)_{Cu} \csc \alpha (\rho t_A)]}{1 - \exp[-(\mu/\rho)_{Ar} \csc \alpha (\rho t_A)]} \quad \cdots \cdots 7.2$$

The equation includes the parameters of:

- Mass absorption coefficient for Ar$_K = (\mu/\rho)_A$
- Mass absorption coefficient for Cu$_K = (\mu/\rho)_Cu$
- Density $= \rho$.
- Detected intensities of Ar and Cu X-rays $= I_{Ar}, I_{Cu}$.
- Percentage of Cu by weight $= C_{Cu}$.
- Percentage of Ar in implanted layer by weight $= C_{Ar}$.
- Cliff-Lorimer factor $= K_{CuA}$.
- Specimen thickness $= t_s$.
- Implanted layer thickness $= t_A$. 
If it is assumed that the overall atomic percentage of copper is the same as that of zirconium we obtain;

\[ A_{Cu} = \frac{1}{2} (1 - A_{Ar}) \]  \[ ....7.3 \]

where A's are the atomic percentages. The atomic percentage of argon can then be calculated from the relation;

\[ A_{Ar} = \frac{C_{Ar} (W_{Cu} + W_{Zr})}{C_{Ar} (W_{Cu} + W_{Zr} - 2W_{Ar}) + 2W_{Ar}} \]  \[ ....7.4 \]

where w's are the atomic masses. Table 7.3 contains the results of applying this relation to several specimens implanted to different doses. Saturation is seen to have occurred at about

1.2x10^17 Ar^+ cm^-2 and the argon content of the implanted layer was ~11.6 at% at this stage.

Saturation occurred at a dose of 1.25x10^17 Ar^+ cm^-2, with a dose rate of 7.94x10^13 Ar^+ cm^-2 s^-1. At this stage ~70nm of material had been removed. This indicates a surface recession rate of 4.63x10^-11 m s^-1. Assuming the material to be CuZr with a density of 7.33 g cm^-3 we have \( S_{CuZr} = 3 \text{ at.ion}^{-1} \).

Using the relation shown in equation 4.11 to correct for the implantation occurring at 45°, we obtain

\( S_{CuZr} = 2.3 \text{ at.ion}^{-1} \). This result is of the same order of magnitude as the results calculated by Matsunami et al [80]. Under the same implantation conditions they found the sputter coefficients for pure zirconium and copper to be 1.9 and 5.5 at.ion^-1 respectively.

At the surface of pure zirconium a layer of zirconia probably exists during bombardment. The value of \( S_{OZr} \) is therefore sensitive to the fact that this layer is present. The fact that \( S_{CuZr} \) is similar to \( S_{OZr} \) suggests that a similar situation exists at the surface of
amorphous CuZr. This supports the theory that zirconium is preferentially sputtered because a thin layer of zirconia rapidly forms at the sputtered specimen surface.

7.2.5 The Development of Bubbles During 80keV Argon Ion Implantation.

A review of TEM applications in the field of ion implantation has been published by Bentley [86]. In this study analytical TEM techniques have been applied to the oxygen uptake and the argon retention of implanted specimens. The images of microstructural changes induced by 80keV argon ions will now be presented. Implantations were performed over a range of doses, but no visible changes occurred until a dose of $6 \times 10^{16}$ Ar$^+$ cm$^{-2}$. At this dose small cavities were visible, although it was difficult to differentiate these features from the mottled contrast associated with the amorphous phase. Some evidence was found that these cavities had a tendency to cluster, as shown in fig.7.24. The cavities were considered to be about to form larger bubbles during a stage of rapid coalescence. Thereafter implantation produced clearly visible cavities. Figs.7.25a to l show specimens in which large bubbles were produced and the associated bubble size distributions. It is interesting to note that there was no evidence of crystallisation in the electron diffraction patterns. Fig.7.25a contains an example of a diffraction pattern taken after implantation. The mottled contrast associated with the amorphous phase was still in evidence around the bubbles. None of the bubbles were faceted as the matrix was essentially homogeneous in terms of surface energy. There was some evidence of bubble coalescence, in that some cavities were
Fig. 7.24. Possible trap clusters in a low-dose specimen.
Diffraction pattern from the specimen imaged below.

Fig. 7.25a. Cavities after $6 \times 10^{16}$ Ar$^+$ cm$^{-2}$. 
Fig. 7.25b. Cavity size distribution for fig. 7.25a.
Fig. 7.25c. Cavities after $8 \times 10^{16} \text{Ar}^+ \text{cm}^{-2}$.
Fig. 7.25d. Size distribution for fig. 7.25c.
Fig. 7.25a. Cavities after $1.5 \times 10^{17} \text{Ar}^+ \text{cm}^{-2}$. 
DISTRIBUTION OF BUBBLE SIZES.

Number Measured: $10^3$
Mean Dimension: $159 \text{Å}$

Fig. 7.25f. Size distribution for fig.7.25e.
Fig. 7.25g. Cavities after $2 \times 10^{17} \text{Ar}^+ \text{cm}^{-2}$. 
DISTRIBUTION OF BUBBLE SIZES.

Number Measured: 806
Mean Dimension: 190.6 Å

Fig. 7.25h. Size distribution for fig. 7.25g.
Fig. 7.25i. Cavities after $2.5 \times 10^{17} \text{Ar}^+ \text{cm}^{-2}$. 
DISTRIBUTION OF BUBBLE SIZES.

Number Measured: 897
Mean Dimension: 191.4 Å

Fig. 7.25j. Size distribution for fig. 7.25i.
non-spherical. This was particularly true at doses above $10^{17}$ Ar cm$^{-2}$.

Appendix B.1 contains a Fortran program devised to process data collected from bubble images. For the purpose of this project two measurements were made on each bubble; these consisted of the magnitude of their longest and shortest chords. This information was used to calculate mean bubble diameters. With the bubble radius a histogram was created to show the distribution of bubble sizes (see fig. 2.5). The following pieces of information were also obtained:

(i) Mean bubble radius and the RMS deviation on this value.
(ii) Mean bubble volume.
(iii) The approximate number of vacancies for this volume.
(iv) The number of gas atoms that would fill these bubbles.
(v) The fraction of the implanted dose found in the bubbles.
(vi) The bubble density.

Over 500 bubbles were measured for each distribution so that the results were statistically representative of the five specimens analysed in this way. The mean number of gas atoms was calculated for each bubble, on the assumption that they were all at equilibrium. That is, the internal bubble pressure was given by $2\gamma/r_b$, with $\gamma=1$ Nm$^{-1}$. This value of $\gamma$ was used because it is typical of crystalline metals. It may well be that this value is incorrect for this metallic glass, but no more appropriate data could be found. Three equations of state were used to make the calculation:

(i) the ideal gas equation;
\[ pv = n_{IC} k_B T \] .......7.5

where \( n_{IC} \) is the number of moles of gas atoms, \( v \) is the bubble volume and \( T \) is the specimen temperature, \( k_B \) is Boltzmann's constant.

(ii) Van der Waal's gas law, in the first approximation;

\[ pv = n_{VDW} (pb + k_B T) \] .......7.6

where \( b \) is a correction for the actual volume of the atoms.

(iii) An interpolated equation generated from data published by Ronchi ['81];

\[ n_R = 10^6 (p-C)v/G \] .......7.7

where \( C \) and \( G \) are interpolated constants with the values \(-1.47 \times 10^9 \text{Nm}^{-2}\) and \(9.33 \times 10^{-14} \text{m}^{-2}\) respectively.

The results of the above calculations are displayed in table 7.3, where the content of gas associated with the observed bubbles is expressed as a fraction of the implanted dose. In addition a further calculation of the argon content of implanted specimens was obtained in section 7.2.4 using EDX analysis. Table 7.4 contains the results of this calculation again in terms of a fraction of the implanted dose.

It can be seen in fig.7.26 that the fraction of the dose to be found in the bubbles calculated by Van der Waal's gas law \( (F_{VDW}) \) and the Ronchi data interpolation \( (F_R) \) agree quite well at low doses. However, the ideal gas law indicates that a far higher fraction of the implanted dose was present \( (F_{IG}) \). When gases are under great pressure the ideal gas law does not describe their behaviour very well. Although the three sets of data are all calculated on the basis that the bubbles are at equilibrium, i.e. their internal pressure can be obtained using \( p=2\sigma/r \), this can lead to high pressures in small cavities
<table>
<thead>
<tr>
<th>Dose (Ar⁺ cm⁻²)</th>
<th>6 × 10¹⁶ (A16)</th>
<th>8 × 10¹⁶ (A11)</th>
<th>15 × 10¹⁷ (A18)</th>
<th>2 × 10¹⁷ (A7)</th>
<th>2.5 × 10¹⁷ (A19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r_b ± σ_r_b (nm)</td>
<td>17.59 ± 5.27</td>
<td>18.81 ± 3.61</td>
<td>18.96 ± 7.21</td>
<td>19.06 ± 10.34</td>
<td>19.14 ± 5.46</td>
</tr>
<tr>
<td>rm (nm)</td>
<td>17.6</td>
<td>18.7</td>
<td>11.6</td>
<td>12.5</td>
<td>15.0</td>
</tr>
<tr>
<td>C_b N 10⁻²¹ (m⁻³)</td>
<td>6.977</td>
<td>6.921</td>
<td>4.466</td>
<td>3.435</td>
<td>3.098</td>
</tr>
<tr>
<td>F_{IG} (%)</td>
<td>105</td>
<td>85</td>
<td>24</td>
<td>22</td>
<td>26</td>
</tr>
<tr>
<td>F_{vdw} (%)</td>
<td>35</td>
<td>28</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>F_R (%)</td>
<td>42</td>
<td>33</td>
<td>12</td>
<td>13</td>
<td>11</td>
</tr>
</tbody>
</table>

r_b Mean bubble radius
σ_r_b RMS deviation on rb
rm Modal bubble radius
Fraction of implanted dose in bubbles, calculated using,

F_{IG} Ideal Gas Law
F_{vdw} Van der Waal's equation
F_R Interpolated Ronchi data.
### TABLE 7.4

<table>
<thead>
<tr>
<th>Dose (Ar⁺ cm⁻²)</th>
<th>AtX ±σ</th>
<th>Atoms per cm⁻² x 10⁻¹⁰</th>
<th>F EDX (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 x 10¹⁶</td>
<td>5.1 ± 1.1</td>
<td>2.04</td>
<td>41 ± 9</td>
</tr>
<tr>
<td>6 x 10¹⁶</td>
<td>6.6 ± 1.4</td>
<td>2.70</td>
<td>45 ± 9</td>
</tr>
<tr>
<td>9 x 10¹⁶</td>
<td>6.6 ± 1.3</td>
<td>2.70</td>
<td>30 ± 6</td>
</tr>
<tr>
<td>12 x 10¹⁷</td>
<td>9.9 ± 1.4</td>
<td>4.05</td>
<td>34 ± 4.8</td>
</tr>
<tr>
<td>1.5 x 10¹⁷</td>
<td>11.3 ± 1.6</td>
<td>4.62</td>
<td>31 ± 4.4</td>
</tr>
<tr>
<td>2 x 10¹⁷</td>
<td>11.5 ± 1.6</td>
<td>4.70</td>
<td>24 ± 33</td>
</tr>
<tr>
<td>3 x 10¹⁷</td>
<td>11.4 ± 1.6</td>
<td>4.66</td>
<td>16 ± 2.2</td>
</tr>
</tbody>
</table>

AtX  Fraction of atoms in implanted region which are argon.

Standard deviation on AtX.

F EDX  Fraction of implanted dose detected by EDX analysis.
Fraction of Dose Retained by Specimens.

Fig. 7.26. The fraction of the implanted dose retained.
so $F_{IG}$ was expected to give a poor measure of the gas content of the foils. At the lowest dose $F_{IG}$ is 105% which is clearly an overestimation. At the lowest doses the fraction of the implanted gas detected by EDX analysis ($F_{EDX}$) is in good agreement with $F_{VdW}$ and $F_R$, suggesting that all the gas was to be found in the bubbles. As the dose increases this agreement becomes worse, with $F_{EDX}$ being consistently greater than $F_{VdW}$ and $F_R$. Indeed $F_{EDX}$ is in better agreement with $F_{IG}$. This suggests that one of the following possible situations had arisen:

(i) A significant fraction of the gas residing in the material was not associated with bubbles, i.e. it was trapped in cavities that were too small to be resolved in the TEM.

(ii) The ideal gas equation became a better approximation to the equation of state of the argon as the dose increased.

To examine the situation further fig. 7.27 was created. This shows the observed slow increase in bubble radius ($r_b$) with dose. Also plotted in this figure are the RMS deviation on $r_b$ ($\sigma_{r_b}$) and the modal (most common) bubble size ($r_m$). It can be seen that the width of the bubble size distribution increases with dose, and that $r_m$ agrees with $r_b$ at low doses. However, $r_m$ becomes significantly less than $r_b$, at a dose similar to that at which saturation took place. Fig. 7.28 contains a plot of bubble density ($\sigma_b$) against dose. This parameter falls continuously with increasing dose.

The onset of saturation in gas content and the beginning of the separation in $r_b$ and $r_m$ seem to occur at approximately the same
Changes in Bubble Size Distribution with Dose.

\[ x = r_b + \sigma_b, \quad a = r_m. \]

**Fig. 7.27.** The increase in \( r_b \) with dose.
The Variation of Bubble Density with Dose.

Fig. 7.28: The bubble concentration as a function of dose.
Fig. 7.29. Surface recession affects the bubble size distribution.
dose. They are both the result of surface recession. Fig.7.29 is a schematic diagram which shows how surface recession might be responsible for the development of the observed bubble distribution. It is assumed that soon after implantation begins a single layer of bubbles develops at the mean range for implanted ions $R_p$. In fig.7.29a bubble layer $L_1$ forms. In fig.7.29b the bubbles in $L_1$ have grown, through the accumulation of gas and free volume, and have moved nearer the specimen surface as a result of surface recession. During the same period $L_2$ has formed. In fig.7.30c some bubbles from layer $L_1$ have been lost through intersection at the specimen surface, $L_2$ has grown and $L_3$ has formed. The process just described leads to a maximum bubble size, which depends on the rate of surface recession and the rate of growth. A consequence of this process is that large bubbles are preferentially removed from the bubble size distribution. These schematics represent a simplification of the actual growth process, as they take no account of the effects of coalescence on the bubble population. However they do serve to emphasise that surface recession will have an influence on the observed distribution.

The observation of non-spherical bubbles at high doses is not the only evidence that bubble coalescence has a part to play in the growth of bubbles. Fig.7.28 contains a plot of bubble density ($\phi_b$) as a function of the implanted dose. It can be seen that $\phi_b$ falls as the dose increases, throughout the range examined. At low doses the slope $d\phi_b/dD$ is extremely steep. It can be estimated that the bubble density soon after nucleation is $2 \times 10^{24} \text{m}^{-3}$. This value was obtained using the gas diffusion coefficient obtained in section 7.2.1 and a bubble radius of 1nm. The high rate at which $\phi_b$ falls at low doses suggests that bubble coalescence is primarily responsible for
growth. This is not surprising as the bubbles are initially small (which means they will be relatively mobile) and close together. The importance of this growth mechanism becomes less as $\alpha_b$ falls and the bubbles become larger on average. As the rate of coalescence decreases other growth mechanisms are expected to become relatively more important.

Another way in which bubble growth could occur is by the accumulation of gas atoms and the relaxation of the surrounding material so that the internal bubble pressure is to some extent relieved. This mode of growth is known to be important in crystalline metals above $0.5T_m$, when the equilibrium density of vacancies is high. It may occur at relatively low temperatures in metallic glasses, i.e. below $T_x$, as excess free volume is a feature of the amorphous state. In addition changes in the amount of excess free volume are known to occur through small atomic rearrangements below $T_x$. The probability of such rearrangements occurring would be enhanced during implantation as a result of radiation enhanced diffusion.

7.2.6 Modelling Growth by Accumulation and Relaxation.

In section 5.8 the bubble growth model developed by Van Swijgenhoven et al was described. In principal, this model is based on the accumulation of gas atoms and free volume. However the treatment requires that the concept of a capture length is applied to free volume in the region of the bubble. In this section an alternative treatment is presented in which the following assumptions are applied:
(i) All gas atoms which arrive within a distance \((1/a_b)^{1/3}\) of a bubble diffuse rapidly to that bubble.

(ii) The rate at which gas atoms reach the bubble as a function of dose is proportional to the volume of metal around each bubble. This is taken to be:

\[
\frac{dn}{dt} = \frac{dD}{dv} dt (c_b^{\frac{1}{3}} - V_b) \quad \ldots \ldots 7.8
\]

where \(V_b\) is the bubble volume. This treatment implicitly assumes that few gas atoms are stopped by the gas already in the bubble. This is likely to be the case for large bubbles at equilibrium, where the gas is under relatively low pressures. This is notably different to the Van Swijgenhoven model, where the gas arrival rate was taken to be proportional to the surface area of the bubble (see equation 5.9).

(iii) All bubbles are at equilibrium pressures, i.e. the internal pressure is opposed by the surrounding material. This assumption is justified because intrinsic and extrinsic free volume is present during implantation, the specimen surface is nearby and is a good source of free volume, and the constant bombardment leads to enhanced diffusion.

(iv) The gas obeys Van der Waal's equation of state;

\[
(p + a/v^2)(v - b) = nk_B T \quad \ldots \ldots 7.9
\]

where \(p\) is the pressure, \(v\) is the volume and \(T\) is the temperature of the gas. \(b\) corrects for the volume of the gas atoms themselves and \(a\) corrects for Van der Waal's interactions between atoms. \(n\) is the number of moles of atoms present and \(k_B\) is Boltzman's constant.

Appendix B.2 contains the computer code applied to this model.
Firstly the number of atoms in the average sized bubble was calculated after a dose of $6 \times 10^{16} \text{Ar}^+ \text{cm}^{-2}$. The number of atoms arriving at this bubble was calculated from the implantation rate, corrected by the fraction of gas retained (see $F_{\text{dW}}$ and $F_R$ in fig. 7.26) and using assumption (i) above. The equilibrium bubble radii were then calculated for a range of doses. The results of this computation are displayed in fig. 7.30, where they are compared with the observed bubble distributions. From this figure it is clear that the average bubble size is not well modelled by the computed data. However, the computed curve falls within the bubble size distribution, even at the highest dose studied. It seems likely that growth by gas accumulation and structural relaxation does occur during the argon ion implantation of amorphous CuZr, but that the distribution of bubble sizes is also affected by bubble coalescence and bubbles intersecting the specimen surface.

This model was also applied to data presented by Van Swijgenhoven et al [83]. The results are presented in fig. 7.31, and it is again clear that the agreement between the experimental data and the calculated curve is poor. In this case however the implanted species was a light ion, and very little material would have been sputtered from the specimen surface. Surface recession was not expected to affect the bubble distribution. The bubbles were small in comparison to the argon results previously modelled, so the rate of coalescence is expected to have been greater for Van Swijgenhoven's data than for the argon data. The rate of coalescence is difficult to estimate because the bubble diffusion coefficient and hence the bubble concentration are dependent on the bubble size. However, assuming that the increase in bubble volume after coalescence is small the following relationship exists between the bubble radius ($r_b$) and the bubble concentration
The Gas Accumulation Model of Bubble Growth.

Fig. 7.30. Comparing the bubble growth model with the experimental data.
The Gas Accumulation Model and Helium Data.

Fig. 7.3: Modelling Van Swijkenhoven's data.

\[ \text{Bubble Radius (nm)} \]

\[ \text{Dose (He}^+ \text{cm}^{-2}) \]

* = Van Swij. et al ["83]

___ = Model Data
\[ C_b r_b^3 = \text{const.} \quad \cdots \quad 7.10 \]

Between doses of 5 and \(10 \times 10^{16} \text{He}^+ \text{cm}^{-2}\), Van Swijgenhoven et al. reported a fall in \(C_b\) from 6 to \(4 \times 10^{24} \text{m}^{-3}\). According to equation 7.10, this should have led to \(r_b\) increasing by a factor of 1.15. In fact, \(r_b\) was reported to increase by a factor of 1.3. This result suggests that a considerable amount of the observed bubble growth should have been attributed to coalescence.

### 7.2.7 Observational Problems in the TEM

A further factor that may have had an influence on the observed bubble size distribution was the difficulty in resolving small bubbles in the TEM. The following reasons for this difficulty were encountered:

(i) To resolve small bubbles, thin specimens are required in which few electrons suffer multiple scattering events. The specimens examined in this part of the project were seldom less than 150nm thick, because the thinnest regions of the thin foil specimens were lost as a result of ion beam erosion during implantation.

(ii) Small bubbles may not have been recorded because they were obscured by the mottled contrast that is associated with the amorphous phase.

(iii) The presence of large cavities made small ones appear insignificant during imaging.
Fig. 7.32. The problem of small cavities.
Fig. 7.32 shows an example of contrast that may have constituted cavities but was not included in the bubble size distributions. The figure consists of an enlarged image of a large bubble, but small features which may have contained gas can be seen in the material between it and the specimen surface.

Some attempt was made to gauge the relative positions of cavities of different sizes within some specimens. Stereoscopic pairs of images were obtained for this purpose. However, as can be seen in fig. 7.33 the bubbles appeared to be arranged in one plane within the depth resolution of the technique. This is not surprising as some of the largest bubbles had a diameter similar in magnitude to \( R_p \).

In the thinnest regions of the implanted foils another interesting effect was observed. An example of what will be termed "crazing" is contained in fig. 7.33. The term craze in this context refers to the channels of light contrast which can only be an indication of thinner areas of specimen. Within these crazes bubbles are visible, but they are smaller than those in the adjacent material. This difference in bubble size is probably the result of the maximum bubble size being limited by the recession rate of the surface. For a more massive incoming particle it seems that the density of crazes increases.

Fig. 7.34 contains an image of a thin region of amorphous CuZr implanted with 80keV krypton ions to a dose of \( 5 \times 10^{16} \text{Kr}^+ \text{cm}^{-2} \).

It is impossible to draw conclusions about craze formation from this small amount of qualitative evidence. However, the following factors are different for the argon and krypton ion implantations, and so may be related to craze formation:
Fig. 7.33. Stereo pair showing cavities distributed through a thin layer.
Fig. 7.34. "Crazes" observed in argon implanted amorphous CuZr.

Fig. 7.35. "Crazes" observed following krypton ion implantation.
(i) The equation of state; stress will be induced in the specimen by the presence of pressurised gas. This leads to compression in the bubble layer and tension in the regions above and below. The induced stress may have been released in these samples by deformation in weak regions, leading to craze formation.

(ii) The projected range; this is lower for krypton than for argon, and as a result the krypton density in the implanted layer is greater than that of argon. This would be influential if crazes were formed through stress relaxation.

(iii) Ion mass; krypton is heavier than argon and so sputters atoms away from the specimen surface at a greater rate. It is difficult to see how this factor would influence the density of crazes, but sputtering may well accentuate the thinning effect at crazes.

Further experiments would be needed to indicate how crazes form. A series of experiments conducted over a range of ion masses may prove conclusive. The phenomenon may be important, as it could be related to lateral stress induced by ion implantation. Lateral stress is thought to be important in the formation of blisters (see section 4.3).
7.3 Helium Ion Implantation of Bulk Specimens.

This study is involved with the formation of blisters on specimens of amorphous CuZr during 100keV helium implantations. The implantation rate was approximately $2 \times 10^{13} \text{He}^+ \text{cm}^{-2} \text{s}^{-1}$ and doses between $10^{17}$ and $10^{18} \text{He}^+ \text{cm}^{-2}$ were used. Specimens were prepared by mechanical polishing down to the 0.25um level, and a brief period of electropolishing in the Tenupol as described in section 6.5. The surfaces were studied in the SEM before and after implantation. Before implantation the specimens were virtually featureless, but some scratches remained from the mechanical polishing away from the center of the electropolished region.

7.4 Blister Formation.

The first surface features related to the ion implantation were observed away from the centre of the specimens at a dose of $2 \times 10^{17} \text{He}^+ \text{cm}^{-2}$. There was some evidence of alignment with these small blisters, probably as a result of being associated with the poor quality of specimen preparation in regions away from the centre of the specimen.

Uniform blister formation in the center of the specimen was first observed at a dose of $4 \times 10^{17} \text{He}^+ \text{cm}^{-2}$, but also occurred in all specimens implanted with higher doses, as is shown in figs. 7.36a to d. The critical blister dose was thus found to be
Fig. 7.36a. Blisters on amorphous CuZr implanted to $4 \times 10^{17} \text{He}^+ \text{cm}^{-2}$. 
Fig. 7.36b. Blisters after $6 \times 10^{17} \text{He}^+ \text{cm}^{-2}$. 
Fig. 7.36c. Blisters after $8 \times 10^{17} \text{He}^+ \text{cm}^{-2}$. 
Fig. 7.36d. Blisters after $10^{18}$He$^+$cm$^{-2}$.
\[ \phi_c = 3 \times 10^{17} \text{He}^+ \text{cm}^{-2} \]. Fig. 5.2 shows how this result compares with other measurements of \( \phi_c \). The figure contains a plot of \( \phi_c \) against energy of implantation for all the metallic glasses that have been investigated in this way. The value of \( \phi_c \) increases with energy, as might be expected for crystalline metals.

Initially small blisters with a diameter of less than 0.5\( \mu \text{m} \) were observed. The areal density of these features was approximately \( 5 \times 10^{13} \text{m}^{-2} \). As the dose was increased to \( 6 \times 10^{17} \text{He}^+ \text{cm}^{-2} \), a population of larger blisters was seen (see fig. 7.36b). These blisters were of the order of 2\( \mu \text{m} \) in diameter. At \( 8 \times 10^{17} \text{He}^+ \text{cm}^{-2} \) the number of large blisters increased, and it appeared that they were forming when the smaller blisters joined up. The highest dose implanted was \( 10^{18} \text{He}^+ \text{cm}^{-2} \). At this dose extremely large blisters were observed, many of which had fractured lids which had exfoliated. Below the exfoliations the specimen surface was seen to have a texture which probably consisted of the remnants of fractured interbubble material and a second phase of blister formation. Efforts were made to measure the blister lid thickness \( (t_b) \) from images taken at high angles of tilt in the SEM. Examples of the images obtained are shown in fig. 7.37. The mean edge thickness was found to be 95\pm10\( \text{nm} \). This value is considerably less than the mean projected range for 100keV helium ions in \( \text{CuZr} \) \( (R_p) \) which is 360\( \text{nm} \). This result is surprising because as discussed in chapter 4 \( t_b \) and \( R_p \) are expected to be similar in value.

Amorphous metals are known to be relatively ductile, and it was therefore possible that while the blister lids were thin near the edges, they were considerably thicker in other regions. To investigate this possibility some exfoliated lids were removed for study in the TEM.
Fig. 7.37. Blister lid edges in the SEM.
Removal was facilitated by a two stage method of surface replication. Firstly, a strip of cellulose acetate was softened and placed on the specimen surface. When the acetate was dry it was peeled away and a layer of carbon was deposited on the surface of the sheet in which blister lids were buried. Subsequently the cellulose acetate was dissolved in acetone vapour, to leave the carbon film supported by a TEM specimen grid. Two examples of lids which were transferred to the TEM by this technique are shown in fig.7.38. These images show that a considerable number of large (~10nm) bubbles had developed in the lid during implantation.

The use of EELS to measure specimen thickness in the TEM was described in section 6.6, and applied several times in the previous sections of results. In this case it was used to estimate the thickness of blister lids away from their edges. The results are displayed in table 7.5, and indicate an average lid thickness of 110±30nm. This result is in good agreement with the edge thickness of the lids, as observed in the SEM. The thickness of the blister lids was therefore uniformly less than the value of $R_p$.

7.5 A Discussion of Blister Formation.

Van Swijgenhoven et al ['84] have already reported that large bubbles form during the helium implantation of amorphous metals to high doses at room temperature. In this publication Van Swijgenhoven et al also noted that the first blisters to be seen were small. However, it was not pointed out that the early stages of blister formation manifest themselves in the form of surface features of similar diameter to the largest bubbles. In
Fig.7.38. Blister lids removed from amorphous CuZr implanted to a dose of \(10^{13}\) He\(^+\)cm\(^{-2}\). Large bubbles are clearly visible.
Table 7.5.

Edge thickness of blister lids obtained by high angle SEM.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
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<tbody>
<tr>
<td>89</td>
<td></td>
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<tr>
<td>102</td>
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<td>108</td>
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<td>97</td>
<td></td>
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<td>111</td>
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Van Swijgenhoven's work low energy (5keV) helium implantations were performed on an amorphous FeNiMoB alloy, and bubbles were observed by electropolishing specimens from the unimplanted surface. During the course of this project helium bubbles were observed in the lids of exfoliated blisters following 100keV helium ion bombardment of amorphous CuZr. The largest cavities were of the order of 0.1 μm in diameter, and so were of similar size to the first surface features to be observed. The next stage of blister development involved the formation of large, rather flat features (see fig. 7.36c). These were qualitatively consistent with the meeting of bubbles below the specimen surface, so that increasingly large areas of the specimen surface lost contact with the bulk of the sample. At the highest dose a large number of the blister lids had become dome shaped or ruptured. It remains to be seen if these effects can be accounted for by the mechanisms for blister formation described in chapter 4.

In fig. 7.39 the results reported in the previous section are plotted on a graph presented by Eer Nisse and Picraux [ '77] in support of their lateral stress mechanism for blister formation. The theoretical lines in the figure were calculated using equation 4.5. It can be seen that the data obtained for amorphous CuZr does not fall within the expected region of the plot. A factor which is unknown and may have had some effect on the blisters formed is the way in which E/σ_y is affected by increased temperature. Increased temperature due to ion implantation may have aided the formation of large bubbles through enhanced atomic diffusion, and reduced the value of σ_y thereby increasing the ratio of d_b to t_b. The effect would have become more pronounced as the thermal contact between the lid material and the bulk became worse.

It is also possible to investigate the possibility that interbubble
Fig. 7.39. Comparing the smallest and largest blisters produced on amorphous CuZr with the model and collated data of Eer Nisse and Picraux.
fracture led to the observed surface features. If equation 4.4 is considered and the following values are used: \( \sigma_y = 1.8 \text{GPa} \) [Cahn '80], \( t_b = 100\text{nm} \) and \( d_b = 100\text{nm} \), the internal bubble pressure required to produce the first observed surface deformations is found to be 4.8GPa. However, as shown in fig.7.38 many bubbles of this diameter are considerably closer to the surface than 100nm. It is these near-surface bubbles that were probably responsible for the observed surface features.

The equilibrium pressure for a bubble of radius 50nm is about 40MPa. Using equation 4.4 again the expected value of \( t_b \) to produce surface deformation is found to be 10nm. This is in better agreement with the TEM observations. The calculation suggests that a significant number of large bubbles are to be found within 100nm of the specimen surface, and that these bubbles are virtually at their equilibrium pressure. The interbubble fracture model of blister formation demands that overpressurised bubbles are present in the region where the material fails. From the above calculations it seems that the bubbles were in fact quite close to equilibrium. From the exfoliated blister lids it was possible to estimate that the near-surface bubble density was \( 8 \times 10^{13} \text{m}^{-2} \). Using this value, \( r_b = 250\text{nm} \) and \( \sigma_y = 1.8 \text{GPa} \) in equation 4.3 indicates that pressures in excess of \( 10^{12} \text{Pa} \) would have been required for the observed bubbles to induce interbubble fracture. This figure is highly unlikely to be correct, so it follows that interbubble fracture was not the dominant mechanism by which the final large blisters formed.

It seems that neither of the commonly presented models of blister formation can explain the effects observed on amorphous CuZr. However, it must again be emphasised that the tensile properties of the implanted region may have been affected by the implantation process. An increase in specimen temperature may have been particularly influential, and may have
occurred despite the fact that each specimen was in good thermal contact with a relatively massive aluminium stage. Specimen heating would have led to an increase in atomic mobility, over and above that possible at room temperature. This would have helped bubbles to grow to large sizes, probably through migration and coalescence and/or the collection of free volume. The fact that significant beam heating occurred after blister formation is supported by the observation that no bubbles are present in the centre of the lid shown in fig. 7.38a. In this region bubble mobility was probably increased to such an extent that all the cavities were lost by intersecting the surface. Any remains of this bubble loss would have rapidly healed through atomic surface diffusion.

In addition, oxygen diffusion into the specimen may also have been induced. This could have resulted in the existence of a weakened interface between oxygen containing and oxygen free metal, and so account for the large discrepancy between $t_b$ and $R_p$.

It is possible that more conventional blister formation had occurred, or was about to occur, with $t_b$ equal to $R_p$. The formation of multiple fracture zones during inert gas ion implantation has been observed in several crystalline metals, although the effect has yet to be adequately explained [Jones and Johnson '86].
Discussion.

The amorphous CuZr alloy was produced by rapid solidification of the melt. A study of literature dealing with the formation of the amorphous phase in alloys suggested that the nature of the material produced by this technique was sensitive to the rate at which cooling occurred. The melt-spun ribbon was therefore investigated in a number of ways to ensure that its properties fitted those of amorphous phases produced by other workers. The techniques of X-ray diffraction, scanning electron microscopy and differential scanning calorimetry showed that the ribbon was amorphous and contained as little oxygen as possible. It was also found that the products of crystallisation which resulted from thermally annealing the bulk material were identical to those reported elsewhere (see chapter 2).

Thin specimens of the amorphous alloy were produced for study in the transmission electron microscope using an electrochemical process. The results were again consistent with those reported by other workers. The presence of oxygen in these specimens was the subject of a detailed investigation. It was found that oxygen was only present in thin layers at the specimen surface; these layers were amorphous. Vitek et al ['75] concluded that they had produced a "transformed amorphous phase" during their electron diffraction studies of amorphous CuZr. From the results presented in this thesis it seems likely that they had in reality detected the presence of an oxygen-containing surface layer.

It is well known that damage can result from the passage of the electron beam through a sample in the TEM. The possibility that amorphous CuZr might suffer such damage was investigated. Beam damage did occur and could be
Discussion.

monitored in terms of oxygen uptake and crystallisation of the specimen. However, to produce these effects a high current density was required in the electron beam. The conditions which produced visible damage were considerably more severe than those used during microanalysis in the TEM. Beam damage during analysis was therefore considered to be insignificant.

Argon ion beam milling was used as an alternative method of specimen production for the TEM. However, the milling process resulted in detectable amounts of argon remaining in each specimen. The retained gas was found to reside in small cavities and the milling process was used to obtain an estimate of the argon diffusion coefficient, $D_A$. $D_A$ was found to have the anomalously high value of $4 \times 10^{-12} \text{cm}^2\text{s}^{-1}$. This high value is likely to have been the result of radiation enhanced diffusion (RED). Oxygen was detected in the ion beam milled samples and was found to reside in surface layers whose thickness was similar to the maximum range of argon ions during implantation. This fact can again be attributed to RED perhaps assisted by oxygen knock-in from the surface. Subsequent annealing of the thinned specimen had no effect on the bubbles that had been produced. It seems likely that the high cavity stability resulted from the presence of oxygen within the specimen.

Electropolished specimens of amorphous CuZr were then implanted with 80keV argon ions and analytical techniques were used to investigate the nature of the implanted region of the specimens. Rutherford backscattering spectroscopy revealed that a near-surface layer had been produced which was significantly richer in copper than the original alloy, and that the thickness of this layer was the same as the maximum range of the implanted ions. The presence of this layer could not be explained by purely kinematical considerations of the surface sputtering process. Instead it seems likely that the effect resulted
from zirconium's high affinity for oxygen. The heat of formation of monoclinic ZrO₂ is \(-263.04\text{kJmol}^{-1}\), while that of the most stable copper oxide Cu₂O is \(-37.6\text{kJmol}^{-1}\). During the oxidation of CuZr alloys zirconia forms at the specimen surface while a copper rich layer forms beneath it. During ion bombardment the zirconia would have been continuously removed but its formation and the sub-surface copper enrichment would also have been continuous. For this to result in the formation of a copper rich layer the zirconia must have initially been produced more rapidly than it could be removed by the sputtering process. In addition the implanted region was found to contain a significant amount of oxygen. This was probably introduced through knock-in from the surface and RED.

Argon ion bombardment resulted in chemical changes within the amorphous CuZr. It also led to microstructural modifications in the form of argon bubbles. These features appeared to nucleate homogeneously and exhibited no faceting because the amorphous alloy was homogeneous, i.e. it had no planes on which surface formation was preferred. Bubbles did not appear until a critical content of 5at% argon was exceeded in the implanted region. Below this critical level, argon resided in traps which were too small to be resolved amongst the mottled contrast which is characteristic of the amorphous phase. Once bubble growth began it proceeded rapidly, probably through a combination of "free volume punching" (by analogy with the athermal process of loop punching observed in crystalline metals) and coalescence. The free volume punching contribution to bubble growth rapidly decreased as the internal bubble pressure was reduced and the amorphous matrix became capable of restraining the gas. Growth by bubble coalescence continued to be important as was evident from the continuous fall in bubble density. It has been suggested by Van Swijgenhoven et al ['84] that bubble growth also occurs by the accumulation of free volume. Van Swijgenhoven et al claimed that the
Discussion.

Bubble size distributions measured following their helium ion implantations of an FeNiMoB amorphous alloy could be explained completely in terms of this process. In this thesis it is suggested that their results are better explained in terms of free volume accumulation combined with bubble coalescence. Their observation of falling bubble density can only be explained in this way.

For the argon implanted specimens it can be shown that approximately 13% of the implanted volume of material was taken up by bubbles. This was significantly more than could have been produced by displacement damage (~5%), which was in turn greater than the intrinsic free volume of the amorphous phase (~2%) [Cahn '80]. The most probable source for the required free volume was the specimen surface. Marochov et al ['87] have shown that the specimen surface acts as the major source of vacancies for bubble growth in nickel above $0.5T_m$, and in the absence of continued irradiation. A similar situation arises in amorphous CuZr at room temperature during implantation.

Despite the fact that bubble growth must involve the movement of enormous numbers of atoms crystallisation was not observed in amorphous CuZr following krypton, argon and helium implantations. Similar observations have been made by other workers for a variety of amorphous alloys. Further, the scale of bubble growth in amorphous alloys during implantation compares with that observed in crystalline metals in the absence of continued implantation, but at temperatures of ~0.5$T_m$. The atomic movement required for bubble growth was probably achieved with the aid of RED. The retention of the amorphous state probably results from the combined effects of displacement damage, which continually introduces disorder, and energy being rapidly dissipated from the region of cascades. It can be estimated that within a
cascade temperatures of the order of 1000K are reached. Under the implantation conditions used during this project this temperature would fall to near-room temperature in less than a nanosecond [Thompson '69]. The effective quench rate in cascades is thus thought to have been much higher than that required to produce amorphous CuZr from the melt. It seems that RED aids the movement of free volume and oxygen into amorphous CuZr. It also aids the movement of argon atoms within the material. However, it does not allow regions of ordered metal atoms to form. To discuss the effect of RED further we must attempt to define it carefully. In a recent publication Johnson ['86] stated that RED involved a cascade from which energy was dissipated, followed by atomic diffusion at rates corresponding to the ambient temperature. This suggests that the only difference between diffusion during implantation and in the absence of implantation is the possibility of atoms being knocked into the specimen. During most implantation experiments specimens suffer a significant increase in temperature. Certainly during this project the specimen holders were not cooled and were warm to the touch when removed from the implant chamber. To investigate the extent to which RED affected the nature of specimens it would be necessary to compare implanted samples with others subjected to an identical thermal history. This could be achieved if some specimens were mounted near the area that was hit by the ion beam. These would reach a similar temperature to the implanted specimens for the same length of time by virtue of the high thermal conductivity of the specimen holder. This experiment was not performed during the course of this project, so no data is available to indicate whether Johnson's description of RED describes the process by which oxygen entered the specimens. It seems likely that the specimens suffered a rise in temperature of approximately 100K. Such a rise combined with the introduction of point defects by radiation damage would have been required to allow argon to diffuse rapidly. Clearly the specimens did not approach $T_x (750K)$ as this would have resulted in
crystallisation despite the high cascade quench rate. If the specimens had not been on average substantially cooler than $T_x$ cascades would not have been quenched rapidly below $T_g$. Having shown that the specimen did not get hotter than 400K it is possible to confirm that RED was necessary for oxygen to penetrate to the measured depths. Guerlet and Lehr ['69] and Darras et al [ '68] measured the diffusion coefficient for oxygen into CuZr alloys at 1050K. The largest diffusion coefficient was less than $10^{-10} \text{cm}^2\text{s}^{-1}$. Over times similar to those required for the implantations such a diffusion coefficient would lead to a penetration of $\sim 10\text{nm}$. This is significantly less than occurred during implantation, and provides an upper limit for oxygen penetration unaided by radiation damage. RED therefore had a significant effect on atomic diffusion within the implanted layer.

Using EDX analysis it was shown that the argon content of the implanted layer reached a maximum value of $\sim 11.6\text{at}\%$. The mechanism of saturation was surface sputtering which resulted in gas release. Two methods were available to estimate the fraction of implanted gas that was retained by samples of amorphous CuZr: (i). EDX (leading to the calculation of $F_{\text{EDX}}$, see fig.7.26) and (ii). bubble measurement. The second of these methods inevitably involved uncertainties as a result of the following aspects of the calculation: (i). An equation of state was required to describe argon under high pressures, (ii). it was impossible to know whether the bubbles were at equilibrium and (iii). whether the extent of overpressurisation was a function of bubble size. It was assumed that all bubbles in the distribution were at equilibrium. The fraction of implanted gas retained was then calculated using the ideal gas equation (to give $F_{\text{IG}}$), Van der Waal's gas law (to give $F_{\text{VDW}}$) and an equation interpolated from calculations by Ronchi ['81] (to give $F_{\text{R}}$). At low doses $F_{\text{EDX}}$ was in good agreement
with $F_{VDW}$ and $F_R$. Ronchi's data is thought to provide a good
approximation for the equation of state of argon under the pressures known to
exist in small cavities. Van der Waal's gas law therefore appears to be quite
accurate under the conditions studied. The results at low doses also lend
support to the assumption that the bubbles are near equilibrium pressures,
because all the detected gas can be accounted for using this assumption. As
the amount of gas implanted was increased $F_{EDX}$, $F_{VDW}$ and $F_R$ all
decreased indicating that saturation was occurring. However, the amount of
gas detected by EDX analysis was greater than that calculated to be in the
measured bubbles. It is likely that this results from a significant amount of
gas residing in unmeasurable traps. These traps were indistinguishable from
the mottled contrast of the amorphous phase. Their formation was probably the
result of incoming gas arriving in regions where no large cavities existed
because bubbles had coalesced or had intersected the surface of the specimen.

Blister formation was not possible during argon ion bombardment because
the specimen was being eroded by sputtering. To investigate blister formation
in amorphous CuZr electropolished samples were implanted with 100keV helium
ions. For these particles the projected range was higher and the rate of
surface erosion far lower than that for argon ions; as a result blisters
formed. The critical dose for blister formation ($\phi_c$) fell in the expected
region of a plot of $\phi_c$ against incident energy for various amorphous
alloys (see fig.5.2). The values on this plot were of the same order of
magnitude as those reported for crystalline metals [Das and Kaminsky '75,
Scherzer '83]. However, the blisters did not develop in a way that might be
expected for crystalline metals implanted at room temperature. Initially
small ($d_b$=0.5um) blisters were formed, with an areal density of
$5 \times 10^{13}$m$^{-2}$. These linked up to produce flat-topped features
($d_b$=2um). In turn these features led to the development of large
(d_b=10um) blisters, many of which had exfoliated. The blister lids were found to be surprisingly thin, and contained large bubbles with an areal density of about 8x10^{13} m^{-2}. This density compares well with that obtained for the initial blister population. Consideration of the pressures required to deform the specimen surface indicated that the initial blistering was caused by large, near surface bubbles, which contained gas under near equilibrium conditions. These bubbles linked up as implantation continued to produce large, thin-lidded blisters.

Neither of the popular models of blister formation can account for these effects, but the following mechanism could account for the formation of a near surface fracture zone. Not only does this mechanism account for the low value of t_b observed for helium implanted amorphous CuZr, but it explains the formation of double fracture zones which have been observed by Jones and Johnson ['86]. Marochov et al ['87] have shown that bubble growth during post-implantation annealing results largely from the accumulation of vacancies which originate from the specimen surface. Fig.3.4 contains a sequence of micrographs showing specimens of helium-implanted nickel which were annealed for increasing periods of time. The near-surface bubbles reached their equilibrium size before those at greater depths began to receive vacancies. In this discussion it has already been proposed that during implantation free volume from the specimen surface was primarily responsible for bubble growth in amorphous CuZr. However, during implantation bubbles are continually receiving gas atoms, as a result they continually require free volume to equilibrate. As long as surface recession were insignificant fig.8.1 would represent bubble growth as a function of time and distance from the specimen surface. The largest bubbles would occur nearer the specimen surface than the projected range (R_p), e.g. at d_{MAX} in fig.8.1. Bubbles on the surface side of d_{MAX} would have most opportunity to receive free volume,
Fig. 8.1. A schematic diagram showing the development of a near-surface fracture zone. The full line represents the gas distribution (maximum bubble pressure occurs near $R_p$). The dotted lines show how the bubble population would evolve with time.
and so would be close to their equilibrium size. Below $d_{\text{MAX}}$ the majority of gas would arrive in the specimen but bubbles would be smaller than their equilibrium size because less free volume would be available.

As implantation continued the average bubble size would rise, but the largest bubbles would always be found near $d_{\text{MAX}}$ not $R_p$. Eventually bubbles at $d_{\text{MAX}}$ would reach a size which was a large fraction of the average interbubble spacing, this would lead to cavity coalescence, and in turn to increased cavity pressure. Catastrophic failure and the formation of blisters with a lid thickness of $d_{\text{MAX}}$ would then occur. This is the process which took place in helium implanted amorphous CuZr.

As long as gas atoms could not readily move from regions near $R_p$ a second fracture zone would occur there, because bubbles in that region would be the most over pressurised. This second fracture zone would lead to blister formation through interbubble fracture or the build up of lateral stress.

It is possible that under certain conditions fracture could take place in both of the regions described above. This provides an explanation for the occurrence of two fracture zones, as observed by Jones and Johnson ['86].
9 Conclusions.

From the results described in this thesis it is possible to draw a number of conclusions about the resistance of amorphous Cu$_{50}$Zr$_{50}$ to radiation damage. These conclusions can be grouped under three headings: "Surface Sputtering", "Inert Gas Bubble Growth During Implantation" and "Blister Formation".

9.1 Surface Sputtering.

1). During 80keV argon ion bombardments at 45° atoms were sputtered away from the surface of amorphous CuZr. The rate of sputter was 2.3at.ion$^{-1}$, which is similar to that expected for zirconium under the same conditions.

2). As a result of Sputtering the gas concentration of the implanted layer saturated. This occurred at approximately 11.6at% of argon.

3). Sputtering led to the formation of a copper rich layer, because a thin layer of zirconia was continually replenished at the specimen surface.

4). It also led to oxygen entering the specimen, probably through the combined effects of oxygen knock-in from the specimen surface and radiation enhanced diffusion.
9.2 Inert Gas Bubble Growth During Implantation.

1). In amorphous CuZr a critical gas content is required before bubble formation occurs. When argon atoms were introduced to the alloy by 80keV ion bombardment the critical content for bubble formation was \( \sim 5\text{at\%} \).
2). The specimen surface acted as a source of free volume.
3). Large bubbles, which were apparently near equilibrium, formed during room temperature implantation. Under these conditions bubble growth was easier in the amorphous alloy than in a crystalline one.
4). In the experimental regime where bubbles could be measured growth was found to take place by a combination of two mechanisms: a) gas atom and free volume accumulation and b) bubble coalescence.
5). Inert gas ion bombardment did not cause the amorphous alloy to crystallise because disorder was continuously introduced. This disorder was retained as the thermal energy associated with cascades was rapidly dissipated, and the specimen temperature did not approach \( T_x \).

9.3 Blister Formation.

1). During 100keV helium implantation of amorphous CuZr blister formation began at a dose of \( 3\times10^{17}\text{He}^+\text{cm}^{-2} \).
2). The first surface deformation was caused by large near-surface bubbles. Gas at equilibrium pressures would have been sufficient to produce the observed surface deformation.
3). The specimen surface provided free volume to the bubble population. A weakened zone developed near the specimen surface as large bubbles
formed.

4). Eventually large thin-lidded blisters formed as a result of this zone being present.

5). The process by which thin-lidded blisters were produced during this project may account for the fracture zones (one near the specimen surface and one near the projected range) observed by Nanao et al ['81] and Jones and Johnson ['86].
## APPENDIX A.1

### Inert Gas on Implantation of TM-M Glasses

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Conditions</th>
<th>Observations</th>
<th>Ref</th>
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</thead>
</table>
| **Pd<sub>80</sub> Si<sub>20</sub>** | 8MeV He<sup>2+</sup> ions  
- φ = 2.5 x 10<sup>14</sup> cm<sup>-2</sup>·s<sup>-1</sup>  
- θ = 2.5 x 10<sup>10</sup> cm<sup>-2</sup>·s<sup>-1</sup>  
- T = 150°C | Little change in X-ray diffraction pattern but slight broadening of peaks noted. | Ayano et al 1979 |
| **Fe<sub>32</sub> Ni<sub>36</sub> Cr<sub>14</sub> P<sub>12</sub> B<sub>6</sub>** | 40KeV He<sup>+</sup> | φ<sub>c</sub> = 1-4 x 10<sup>17</sup> cm<sup>-2</sup>  
Similar φ<sub>c</sub> for Nb & Mo  
- d<sub>b</sub> = 2-4 mm | Carter and Grant 1981 |
| **Fe<sub>50</sub> Ni<sub>50</sub> B<sub>20</sub>** | 2-20 KeV He<sup>+</sup>  
- φ = 9 x 10<sup>18</sup> cm<sup>-2</sup>  
T = 130 - 430 K | Sputter yield at least 3x lower than inconel stainless steel, Fe & Ni. No blistering for Eo 12 KeV  
18 KeV, φ<sub>c</sub> = 8 x 10<sup>17</sup> cm<sup>-2</sup> 1mm blisters | Emmoth et al 1981 |
| **Fe<sub>50</sub> B<sub>20</sub>, Fe<sub>78</sub> Mo<sub>2</sub> B<sub>20</sub>** | 1.5 MeV Ar<sup>+</sup>  
5 KeV Ar<sup>+</sup>  
- φ = 10<sup>16</sup>  
- q<sub>c</sub> = 7.10<sup>16</sup>  
- bubbles r<sub>b</sub> = 1mm | | Grundy et al 1983 |
| **Fe<sub>40</sub> Ni<sub>40</sub> P<sub>14</sub> B<sub>6</sub>** | 40 KeV He<sup>+</sup> ions  
T = 400°C | Crystallisation occurred during implantation, Hayashi & Tabahashi high T could be responsible, but a different phase was produced by annealing alone. d<sub>b</sub> 24 um for blisters. | | |
| **Fe<sub>40</sub> Ni<sub>40</sub> P<sub>14</sub> B<sub>6</sub>** | 40 KeV He<sup>+</sup> | φ = 1.6 x 10<sup>18</sup> cm<sup>-2</sup> - crystallisation blistering and exfoliation.  
- φ = 1.6 x 10<sup>18</sup> cm<sup>-2</sup> - repetitive blistering and exfoliation.  
Cryst. phases observed in damaged region different from annealed samples. | Hayashi et al 1983a |
| **He<sup>+</sup> ions** | Compared RDF before and after irradiation. | | Hayashi et al 1983b |
| **Ni<sub>88</sub> Si<sub>20</sub> Br<sub>4</sub>**  
**Ni<sub>40</sub> Fe<sub>50</sub> Si<sub>20</sub>**  
**Ni<sub>82.4</sub> (CresSiB) 17.6** | 250 eV-8KeV He<sup>+</sup>  
- φ < φ<sub>c</sub> = 2 x 10<sup>7</sup> cm<sup>-2</sup>  
Bubbles observed r<sub>b</sub> = 1 - 4 nm  
No blisters for 250 eV. Eo 8KeV Ni & 316 steel - r<sub>b</sub> 25 nm | | Jaeger & Roth 1981 |
| **Pd<sub>80</sub> Si<sub>20</sub>** | 285 MeV Kr<sup>+</sup> | Dramatic growth perpendicular to implant, no appreciable volume change or micro-structural change. | Klaumunzer & Schumar 1983 |
| **Pd<sub>80</sub> Si<sub>20</sub>, Cu<sub>50</sub> Br<sub>50</sub>** | | | Klaumunzer et al 1982a |
| **Pd<sub>80</sub> Si<sub>20</sub>, Cu<sub>60</sub> Br<sub>50</sub>** | 25 - 250 MeV O<sup>2</sup>-, Ar<sup>+</sup>, Kr<sup>+</sup>  
T = 50 - 140K | Low energy & fluence - increased resistivity Klaumunzer et al almost complete reverse at 400K.  
High fluences - swelling. | Klaumunzer et al 1982b |
| **11 Glasses** | 360 MeV Xe<sup>+</sup>  
- φ = 2.2 x 10<sup>12</sup> cm<sup>-2</sup>  
- T = 20 - 415K | Large anisotropic changes in dimension of sample. Most pronounced at low temperatures. | Klaumunzer et al RQM 5 |
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Conditions</th>
<th>Observations</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{80}$ B$</em>{20}$, Pd$<em>{80}$ Si$</em>{20}$</td>
<td>400 KeV He$^+$ &amp; Ar$^+$ $\phi$ to $10^{18}$ cm$^{-2}$</td>
<td>He - blisters &amp; flakes with double layer structure. Ar - many small pores at surface, similar to hot crystalline metal. 100KeV 2 x $10^{17}$ cm$^{-2}$ - $r_b$ = 5 nm $\phi$ = $8.6 \times 10^{17}$ cm$^{-2}$</td>
<td>Nandao et al 1981</td>
</tr>
<tr>
<td>Ni$<em>{45}$ Fe$<em>5$ Co$</em>{20}$ Cr$</em>{10}$ Mo$<em>4$ B$</em>{16}$</td>
<td>$\phi$ = 3 x $10^{15}$ cm$^{-2}$</td>
<td>Small bubbles grow to deform surface plastically for blister formulation, $\phi_c = 4 \times 10^{17}$ cm$^{-2}$</td>
<td>Nandedkar et al 1981a</td>
</tr>
<tr>
<td>Fe$<em>{80}$ B$</em>{20}$ Ni$<em>{36}$ Fe$</em>{16}$ Fe$<em>{32}$ Ni$</em>{36}$ Cr$_{16}$ B$_6$</td>
<td>50 KeV He$^+$ T = 300 K</td>
<td>Small bubbles grow to deform surface plastically for blister formulation, $\phi_c = 4 \times 10^{17}$ cm$^{-2}$</td>
<td>Nandedkar &amp; Tyagi 1981b</td>
</tr>
<tr>
<td>Fe$<em>{80}$ B$</em>{20}$ Ni$<em>{36}$ Fe$</em>{16}$ Fe$<em>{32}$ Ni$</em>{36}$ Cr$_{16}$ B$_6$</td>
<td>2 MeV He$^+$ $\phi$ = 4 x $10^{17}$ cm$^{-2}$</td>
<td>Surface pattern formation after flaking. No patterns noted after irradiation of equilibrium phase.</td>
<td>Paszti et al 1983a</td>
</tr>
<tr>
<td>Fe$<em>{80}$ B$</em>{20}$ Ni$<em>{36}$ Fe$</em>{16}$ Fe$<em>{32}$ Ni$</em>{36}$ Cr$_{16}$ B$_6$</td>
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<td>Ni$<em>{45}$ Fe$<em>5$ Co$</em>{20}$ Cr$</em>{10}$ Mo$<em>4$ B$</em>{16}$</td>
<td>2 MeV He$^+$ $\phi$ = 4 x $10^{17}$ cm$^{-2}$</td>
<td>Surface pattern formation after flaking. No patterns noted after irradiation of equilibrium phase.</td>
<td>Paszti et al 1983a</td>
</tr>
<tr>
<td>Pd$<em>{80}$ Si$</em>{20}$ Cu$<em>{50}$ Br$</em>{50}$</td>
<td>285 MeV Kr$^+$ 170 MeV Ar$^+$</td>
<td>Radiation induced specimen growth above $1.2 \times 10^{14}$ cm$^{-2}$. Little structural change noted in x-ray studies.</td>
<td>Schumacher et al 1984</td>
</tr>
<tr>
<td>Pd$<em>{80}$ Si$</em>{20}$</td>
<td>140 -170 MeV Ar$^+$ $\phi$ = 3 x $10^{15}$ cm$^{-2}$</td>
<td>Increased electrical resistancy annealed out at 150°C.</td>
<td>Schumacher et al 1980</td>
</tr>
<tr>
<td>Fe$<em>{80}$ B$</em>{20}$ Fe$<em>{40}$ Ni$</em>{40}$ B$<em>{20}$ Fe$</em>{40}$ Ni$<em>{38}$ Mo$<em>4$ B$</em>{18}$ Fe$</em>{40}$ Ni$_{38}$ Mo$<em>4$ B$</em>{18}$</td>
<td>He$^+$</td>
<td>Blister formation from $d_b = 2$-5 mm. Some evidence of lined up blisters, probably as a result of specimen preparation. $\phi_c = 10^{17}$ at 20 KeV, $\phi_c = 4 \times 10^{17}$ at 150 KeV. $\phi_c$ decreases with increased current density.</td>
<td>Tyagi &amp; Nandedkar 1981</td>
</tr>
<tr>
<td>Fe$<em>{40}$ Ni$</em>{38}$ Mo$<em>4$ B$<em>8$ Fe$</em>{40}$ Ni$</em>{40}$ F$<em>{14}$ B$<em>6$ Fe$</em>{40}$ Ni$</em>{40}$ F$_{14}$ B$_6$</td>
<td>20-150 KeV He$^+$ $\phi$ = 3 x $10^{15}$ cm$^{-2}$ $d_b = 0.1 - 0.2$ um $T_c = 300$ K</td>
<td>Blister formation from $d_b = 2$-5 mm. Some evidence of lined up blisters, probably as a result of specimen preparation. $\phi_c = 10^{17}$ at 20 KeV, $\phi_c = 4 \times 10^{17}$ at 150 KeV. $\phi_c$ decreases with increased current density.</td>
<td>Tyagi &amp; Nandedkar 1981</td>
</tr>
<tr>
<td>Ni$<em>{45}$ Fe$<em>5$ Co$</em>{20}$ Cr$</em>{10}$ Mo$<em>4$ B$</em>{16}$</td>
<td>5 KeV He$^+$ T = 300 K</td>
<td>Blister formation from $d_b = 2$-5 mm. Some evidence of lined up blisters, probably as a result of specimen preparation. $\phi_c = 10^{17}$ at 20 KeV, $\phi_c = 4 \times 10^{17}$ at 150 KeV. $\phi_c$ decreases with increased current density.</td>
<td>Van Swijgenhoven 1982</td>
</tr>
<tr>
<td>Ni$_{38}$ Mo$<em>4$ B$</em>{18}$</td>
<td>5 KeV He$^+$ T = 300 K</td>
<td>Blister formation from $d_b = 2$-5 mm. Some evidence of lined up blisters, probably as a result of specimen preparation. $\phi_c = 10^{17}$ at 20 KeV, $\phi_c = 4 \times 10^{17}$ at 150 KeV. $\phi_c$ decreases with increased current density.</td>
<td>Van Swijgenhoven 1982</td>
</tr>
<tr>
<td>Alloy</td>
<td>Conditions</td>
<td>Observations</td>
<td>Ref</td>
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<tr>
<td>Fe\textsubscript{38} Ni\textsubscript{40} Mo\textsubscript{4} B\textsubscript{18}</td>
<td>5 KeV He\textsuperscript{+} ( T = 200 - 600 \text{ K} )</td>
<td>Blister formation may not be due to intebubble fracture, particular above room temperature. May be due to bubble coalescence rather than catastrophic failure of material.</td>
<td>Van Swijgenhoven et al 1983a</td>
</tr>
<tr>
<td></td>
<td>200 - 600 K</td>
<td></td>
<td>Van Swijgenhoven et al 1983b</td>
</tr>
<tr>
<td></td>
<td>5 KeV He\textsuperscript{+} ( \phi = 5 \times 10^{16} \text{ cm}^{-2} \text{s}^{-1} ) ( 0 = 10^{14} - 10^{16} \text{ cm}^{-2} )</td>
<td>50% He retention - bubbles ( \phi = 5 \times 10^{16} ) ( 0 = 10^{14} - 10^{16} \text{ cm}^{-2} ) ( 5 \times 10^{14} \text{ cm}^{-2} ) ( 2 \times 10^{17} ) ( 10^{18} )</td>
<td>Van Swijgenhoven et al 1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Large blisters produced despite the fact that &quot;heavy&quot; ions and 45° angle of incidence we used. Blister density lower than for cryst alloys. ( \phi = 2.4 \times 10^{17} \text{ cm}^{-2} )</td>
<td>Van Swijgenhoven et al 1981</td>
</tr>
<tr>
<td>Fe\textsubscript{80} B\textsubscript{20}</td>
<td>100 - 300 KeV He\textsuperscript{+} ( T = 300 \text{ K} )</td>
<td>( \phi = 5.4 \times 10^{17} \text{ cm}^{-2} ) for 100 KeV He\textsuperscript{+} ( \phi = 2.1 \times 10^{18} \text{ cm}^{-2} ) for 300 KeV</td>
<td>Watanabe et al 1984</td>
</tr>
<tr>
<td></td>
<td>( T = 300 \text{ K} )</td>
<td>Bubbles ( r_b = 5 - 15 \text{ nm} ) Some irradiation induced crystallisation.</td>
<td></td>
</tr>
</tbody>
</table>
## Inert Gas on Implantation of TMC Glasses

### Alloy Conditions Observations Ref

<table>
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<tr>
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</thead>
</table>
| Ni<sub>33</sub> Zr<sub>67</sub> | 100 KeV He<sup>+</sup> Ar<sup>+</sup>  
\( \Phi = 6 \times 10^{16} \text{ cm}^{-2} \)  
\( 6 \times 10^{18} \text{ cm}^{-2} \)  
T = 300 K | \( \Phi = 5 \times 10^{17} \text{ cm}^{-2} \)  
Blisters \( d_b = 1 - 3 \text{ um} \), exfoliated blisters  
much larger. Crystallisation observed.  
Bubbles smaller for He implants than for Ar under similar conditions.  
Ar - 3.25 - 20 nm bubbles. | Tyagi et al 19: |

| Ni<sub>60</sub> Nb<sub>40</sub> Ni<sub>64</sub> Zr<sub>36</sub>  
Ni<sub>33</sub> Zr<sub>67</sub> | 50 - 150 KeV He<sup>+</sup> Ar<sup>+</sup>  
T = 300 K | Ni<sub>60</sub> Nb<sub>40</sub> and Ni<sub>64</sub> Zr<sub>36</sub> showed higher  
resistance to blistering and flaking than other alloys, and did not show signs of  
radiation induced crystallisation.  
\( \Phi \) for 100 KeV He<sup>+</sup> ranges  
1 - 1.6 \( \times 10^{18} \text{ cm}^{-2} \)  
Helium bubbles: \( r_b = 1 - 3 \text{ nm} \)  
Argon Bubbles: \( r_b = 5 - 25 \text{ nm} \) | Tyagi et al 1 |

Helium bubbles: \( r_b = 1 - 3 \text{ nm} \)  
Argon Bubbles: \( r_b = 5 - 25 \text{ nm} \)
# APPENDIX A.3

## Heavy Metal Ion Implantation of Metallic Glasses

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Conditions</th>
<th>Observations</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{40}$ Ni$</em>{38}$ Nb$_{18}$</td>
<td>500 KeV Ni$^+$ $\phi = 6 \times 10^{16}$ cm$^{-2}$</td>
<td>T$_c$ reduced from 350°C to 100-150°C.</td>
<td>Azem et al. 1979</td>
</tr>
<tr>
<td>Mo Ni</td>
<td>5 MeV Ni$^{2+}$ $T = 78$ K</td>
<td>T 570 K crystalline phase – amorph.</td>
<td>Brimhall et al.</td>
</tr>
<tr>
<td>Ni$<em>{60}$ Nb$</em>{40}$</td>
<td>3 MeV Ni$^+$ $\phi = 3 \times 10^{-3}$ dpa s$^{-1}$</td>
<td>T 570 K amorph phase – crystalline.</td>
<td>Rechtin et al</td>
</tr>
<tr>
<td>Ni$<em>{60}$ Nb$</em>{40}$</td>
<td>3.5 MeV Ni$^+$ $3 \times 10^{-3}$ dpa s$^{-1}$</td>
<td>T = 900 K crystalline phase – amorphous under low damage i.e. 1 - 2 dpa</td>
<td>Rechtin et al</td>
</tr>
<tr>
<td>Fe$<em>{40}$ Ni$</em>{40}$ P$_{14}$ B$_6$</td>
<td>60 MeV Ni$^+$ $T = 300$ K</td>
<td>Swelling observed $\phi = 8 \times 10^{15}$ cm$^{-2}$ $\phi = 9 \times 10^{16}$ cm$^{-2}$</td>
<td>Tai-an-Chang. 1977</td>
</tr>
</tbody>
</table>
## APPENDIX A.4

### Electron Bombardment of Metallic Glasses

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Conditions</th>
<th>Observations</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{75}$ B$</em>{25}$</td>
<td>e$^-$ T = 21 K</td>
<td>Displacement energy same in amorphous and crystalline alloys. Recombinations: amorphous - $61 \pm 16$ atom volumes. Crystalline - $130 \pm 32$ atom volumes.</td>
<td>Andouard et al 1982</td>
</tr>
<tr>
<td>Fe$<em>{40}$ Ni$</em>{40}$ P$_{14}$ B$_6$</td>
<td>1 MeV e$^-$ $\phi = 7.5 \times 10^{18}$ cm$^{-2}$s$^{-1}$</td>
<td>Crystallisation occurred through beam heating, Barbu &amp; Limoge not at result of damage. However, density of crystals high, suggesting irradiation enhances bulk diffusion rates.</td>
<td>Brimhall 1983</td>
</tr>
<tr>
<td>Pd Ni Si</td>
<td>1 MeV e$^-$ $\phi = 5 \times 10^{18}$ cm$^{-2}$ T = 300 K</td>
<td>No observed effects.</td>
<td>Chuang et al 1976</td>
</tr>
<tr>
<td>Ni$<em>{75}$ B$</em>{17}$ Si$<em>8$ Ni$</em>{75}$ B$_{15}$ Si$_8$ C$_2$</td>
<td>1 MeV e$^-$</td>
<td>No effect on crystal growth rate or crystal morphology, but increased rate of nucleation.</td>
<td>Doi &amp; Imura 1980</td>
</tr>
<tr>
<td>Ni$<em>{45}$ Fe$<em>5$ Co$</em>{20}$ Cr$</em>{10}$ Mo$<em>4$ B$</em>{16}$</td>
<td>3.5 MeV e$^-$ $\phi = 10^{14} - 4 \times 10^{16}$ cm$^{-2}$ T = 273 K 1 MeV e$^-$ $\phi = 2 \times 10^{21}$ cm$^{-2}$ T = 323 K</td>
<td>No notable effect on Tc. Some change in resistivity - temperature plot.</td>
<td>Nandedkar and Ty 1981a</td>
</tr>
<tr>
<td>Alloy</td>
<td>Conditions</td>
<td>Observations</td>
<td>Ref</td>
</tr>
<tr>
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</tr>
</tbody>
</table>
| Fe₈₀ B₂₀                      | Fast n's  
T = 28 K | Position annihilation indicated increased free volume in structure. Defects were lost in a smooth way between 77 & 300 K.  | Andouard et al 1983a |
| Fe₃₀ B₂₀                      | n's                 |                                                                             | Andouard et al 1983b |
| Fe B Fe B                     | Fast n's  
T = 30 K | Electrical resistivity increased by irradiation. Increase saturated at lower dose than in crystalline metals. | Andouard et al 1979 |
| Ni₄ Zr₃₆                      | Fast & thermal n's  
ϕ = 11 x 10¹⁹ cm⁻² | DSC - pre-crystallisation heat release.  
Probably due to structural relaxation. | Cahn et al 1981 |
| Ti₅₀ Be₄₀ Br₁₀                | n's                 | Sharpening of Ziman structure factor indicated increased atomic mobility during irradiation. | Caton et al 1980 |
| Fe₄₀ Ni₄₀ P₁₄ B₆              | 0.12 MeV N's  
ϕ = 1.2 x 10¹⁹ cm⁻²  
T = 45°C | Pre-irradiation arreal created brittle sample, irradiation - increased ductility. | Chine et al 1981 |
| "                             | "                  | X-ray diffraction indicated no crystallisation or oxidation had occurred.     | Cline et al 1983 |
| Pd₈₀ Si₂₀                    | 1 MeV n's  
ϕ = 5 x 10²⁰ cm⁻² | x-ray diffraction suggested increased disorder after irradiation.  
Glass transition temperature increased by 10 K. | Doi et al 1979 and 1977 |
| (Mo₀.₆ Ru₀.₄)₈₂ B₁₈          | Fast n's  
ϕ = 10¹⁸ cm⁻²  
Low T | Increased superconducting transition temperature  
6.05 - 6.19 K. Density decreased, x-ray peaks broadened. Improved ductility. All suggest defects created at atomic scale. | Kramer and Johns 1979 |
| Pd Si                         | n's                 | Resistivity increased by reduced again by raising specimen to 300 K.          | Takamura and Kobiyama 1984 |
To calculate the distribution of bubble sizes.

CAS = ME or MH (input form e.g.'AM')
DOS = dose in number/cm-2
SHAPE = 'SPHERES' or 'FACETED'
MAC = magnification
SAM = sample identification (two characters only e.g.'A7')
AREA = measured area on prints in cm2
K = number of measurements (2 per bubble for SPHERES, 3 per bubble for FACET)
TIME = time of anneal in hours
TEMP = temp of anneal in Kelvin
STEP = histogram interval in mm

$INSERT BUBCON
CALL READIN
CALL HEAR
CALL SCALE
IF(SHAPE.EQ.'SPHERES') THEN
   CALL SPHERI
ELSE
   CALL FACETE
ENDIF
CALL ORDER
CALL MEANS
CALL HISTNS
CALL RESULT

WRITE(1,*) ('ENTER SCALE FACTOR FOR HIST, BETWEEN 0 AND 1.0')
READ(1,*) U  /* scale factor for final plot.
NBIN = NINT + 1  /* to adjust for grahis.
CALL TTY72  /* hist output routine call to screen.
CALL PLOT
CALL OPMP$A('Enter Filename for Histogram',28,2,NA,20,5)
CALL HV722S
CALL PLOT
WRITE(1,*) ('INPUT YES IF YOU WANT TO PLOT AGAIN, NO IF HAPPY.')
READ(1,*) UNHAP
IF ( UNHAP .EQ. 'YES' ) GO TO 999
WRITE(1,*) (' BEST TO ERASE HIST.BIN, #HIST NOW,THEN CLOSE ALL.')

END

SUBROUTINE PLOT
$INSERT BUBCON
CALL UNITS(U)
CALL WINDO2(0., 225., 0., 300.)
CALL PENSEL(1,0.,0)
CALL AXIPOS(1, 20., 25., 160., 1)
CALL AXIPOS(1, 20., 25., 180., 2)
CALL AXISCA(5, NBIN, 0., XMAX, 1)
CALL AXISCA(1, 10., 0., YMAX, 2)
CALL AXIDRA(1, 1, 1)
CALL AXIDRA(-1, -1, 2)
CALL GRAHIS(TOT, NBIN, 1.0)
IF(U.LT.0.75) GOTO 100
CALL MOVT02(10.,60.)
CALL CHAANG(90.)
CALL MOVT02(60.,10.)
CALL CHAANG(0.)
IF(SHAPE.EQ.'SPHERES') THEN
CALL CHAHOL('Bubble Dimension (Angstroms).')
ELSE
   CALL CHAHOL('Bubble Dimension (Angstroms).')
ENDIF
CALL MOVTO2(50.,210.)
CALL CHAHOL('DISTRIBUTION OF BUBBLE SIZES.*')
CALL MOVTO2(50.,206.)
CALL MOVTO2(100.,190.)
CALL CHAHOL('----------------------------*')
CALL MOVTO2(50.,206.)
CALL MOVT02(100.,180.)
CALL CHAH0L('  Number Measured; *  .  ')
CALL MOVTO2(  100.,180.)
CALL CHAHOL('Mean Dimension;*.')
100 CALL DEFEND
RETURN
END
C
C
SUBROUTINE READIN
$INSERT SUBCON:
READ(6,*) GAS,DOS,SHAPE,MAG,SAM,AREA,N,TIME,TEMP,STEP
READ(6,*)(X(I),1=1,N)  /* X's are diameters for SPHERE.*/
CLOSE(6)
RETURN
END
C
SUBROUTINE HEAR
C
C routine to input data for He or Ar (VDW's equation....)
C
$INSERT SUBCON
IF ( GAS .EQ.'HE'  )  THEN
   B =  4.48E-29
ELSE
   B =  4.48E-29
ENDIF
RETURN
END
C
SUBROUTINE SCALE
C
diameters from READIN scaled here.
C convert X's to real SI units..
C adjusts area, thickness (TH), volume and dose of specimen.
C
$INSERT SUBCON:
DO 10 I=1,N
   X(I) = X(I)*1E-4/HAG
10 CONTINUE
AREA1 = AREA * 1E-4/MAG**2
WRITE(1,*)( 'INPUT THICKNESS OF SPEC. IN ANGS.' )
READ(1,*) TH
TH = TH*1E-10
VOL = AREA1 * TH
ADOS = DOS * 1E4
RETURN
END
C
BLOCK DATA
C GAMMA surface energy, AVOL atomic volume.
C G and C are gradient and constant of RONCHI slope, see PJG.
C K Boltzmann's constant.

DATA GAMMA,AVOL,C,G/1.9,5.848E-24,-1.47E9,9.33E-14/
DATA PI,K/3.1416,1.388-23/
END

C

SUBROUTINE SPHERE

$INSERT BUBCOM

N=N/2
DO 10 I=1,N
R(I) = ( X(2*I) + X(2*I-1) )/2 /* mean diameter.
R(I) = R(I)/2 /* mean radius of each bubble.
V(I) = 4*PI*( R(I)**3 )/3
P(I) = 2*GAMMA/R(I) /* approx. pressure in each bubble.
NIG(I) = ( P(I)*V(I) )/( K*TEMP ) /* ideal gas law.
NDW(I) = ( P(I)*V(I) )/( P(I)*B + K*TEMP ) /* VDW's gas law.
NRGCH(I) = 1E6* ( P(I)-C ) * V(I)/G /* Ronchi data by PJG.
10 CONTINUE
RETURN
END

C

SUBROUTINE FACET

$INSERT BUBCOM

N=N/3
DO 10 I=1,N
V(I) = X(3*I) * X(3*I-1) * X(3*I-2) /* mean dimension of faceted bubble.
R(I) = V(I)**0.333333 /* mean radius of each faceted bubble.
C
P(I) = 4*GAMMA/R(I)
NIG(I) = ( P(I)*V(I) )/( K*TEMP ) /* ideal gas law.
NDW(I) = ( P(I)*V(I) )/( P(I)*B + K*TEMP ) /* VDW's gas law.
NRGCH(I) = 1E6* ( P(I)-C ) * V(I)/G /* Ronchi data by PJG.
10 CONTINUE
RETURN
END

C

SUBROUTINE ORDER

C sorts mean dimensions into ascending order.

$INSERT BUBCOM

DO 20 J=1,N
AMAX = 0
F = 0
DO 10 I=1,N-J
IF( R(I+1) .GE. R(I) ) GO TO 10
AMAX = R(I)
R(I) = R(I+1)
R(I+1) = AMAX
10 CONTINUE
IF ( F.EQ.0 ) GO TO 30
20 CONTINUE
30 RETURN
END

C

SUBROUTINE MEANS

$INSERT BUBCOM
CALL SUMIT( NIG,N )  /* calculates approx. IG dose.  
ANIG = SUM/VOL 
FIG = SUM * 100/( AREA1 * ADOS ) /* fraction of actual dose.  
CALL SUMIT( NIGC,N )  
ANIGC = SUM/VOL 
FRC0C = SUM * 100/( AREA1 * ADOS ) 
RETURN 
END

C
SUBROUTINE SUMIT( IVAL,M )  
$INSERT SUBCON. 
SUM = 0 
DO 10 I=1,M 
   SUM = SUM + IVAL(I) 
10 CONTINUE 
RETURN 
END

C
SUBROUTINE HISTNS  
C
C finds range of data and puts bubble sizes into histogram form.  
C
$INSERT SUBCON.
WRITE(10,*) ('ENTER THE NUMBER OF BIG BUBBLES TO DISREGARD.') 
READ(10,*) ND 
IF( R(N-ND) .LT. 320E-10 ) THEN 
  XMAX = 320 
ELSEIF( R(N-ND) .GE. 320E-10 ) .AND. ( R(N-ND) .LT. 440E-10 ) THEN 
  XMAX = 440 
ELSEIF( R(N-ND) .GE. 440E-10 ) .AND. ( R(N-ND) .LT. 680E-10 ) THEN 
  XMAX = 680 
ELSEIF( R(N-ND) .GE. 680E-10 ) .AND. ( R(N-ND) .LT.1000E-10 ) THEN 
  XMAX = 1000 
ENDIF 
C
LIN1 = 0 
LIN2 = 0 
YMAX = 0 
WRITE(10,*) ('ENTER THE NUMBER OF HISTOGRAM BINS REQUIRED.') 
READ(10,*) HINT 
WRITE(7,*) ('% of Bubbles in the Given Size Range.') 
WRITE(7,*) ('-----------------------------------------------') 
DO 10 I=1,HINT 
   T = 0 
   LIN1 = (I-1) * XMAX * 1E-10/HINT 
   LIN2 = I * XMAX * 1E-10/HINT 
   DO 20 J=1,N-ND 
      IF( R(J) .GT. LIN1 ) .AND. ( R(J) .LE. LIN2 ) T=T+1 
20 CONTINUE 
TOT(I) = 100 * T/N 
IF( TOT(I) .GT. YMAX ) YMAX=TOT(I) 
WRITE(7,*) TOT(I),(' % between'),LIN1,' m. and',LIN2,' m.') 
10 CONTINUE 
RETURN 
END
SUBROUTINE INSERT BUBCON

PRINT*,
WRITE(7,*), '-----------------------------------'
PRINT*,
WRITE(7,*), 'Sample Label;', SAM
IF(SHAPE.EQ.'SPHERES') THEN
   WRITE(7,*), ('No. of SPHERICAL Bubbles;', N)
ELSE
   WRITE(7,*), ('No. of FACETED Bubbles;', N)
ENDIF
WRITE(7,*), ('Dose of ', ' Gas;', DOS, (' cm-2.'))
WRITE(7,*), ('Time of Anneal;', TIME, (' Hours.'))
WRITE(7,*), ('Temperature of Anneal;', TEMP, (' K.'))
WRITE(7,*), ('Magnification;', MAG, (' Times.'))
WRITE(7,*), ('No. of Faceted Bubbles;', N)
WRITE(7,*), ('Specimen Studied;', AREA1, (' m2.'))
WRITE(7,*), ('Thickness of Specimen;', TH, (' A.'))
WRITE(7,*), ('No. of Histogram Bins;', HINT)
WRITE(7,*), ('Surface Energy;', GAMMA, (' Ha-1.'))
WRITE(7,*), ('Atomic Volume;', AVOL, (' m3.'))
PRINT*,
WRITE(7,*), '-----------------------------------'
PRINT*,
WRITE(7,*), ('Mean Bubble Dimension;', AR, ('m.'))
WRITE(7,*), ('Mean Bubble Volume;', AV, ('m3.'))
WRITE(7,*), ('Approx. No. of Vacancies;', NVAC)
WRITE(7,*), ('No. of Gas Atoms from IDEAL GAS LAW;', ANIG)
WRITE(7,*), ('IDEAL GAS -> Fraction of Original Dose;', FIG, ('%.'))
WRITE(7,*), ('No. of Gas Atoms from VAN DER WAALS GAS LAW;', ANVDW)
WRITE(7,*), ('VDW LAW -> Fraction of Original Dose;', FVDW, ('%.'))
WRITE(7,*), ('No. of Gas Atoms from RONCHI DATA;', ANRONC)
WRITE(7,*), ('RONCHI -> Fraction of Original Dose;', FRONC, ('%.'))
END
C FIRSTLY TO CALCULATE NUMBER OF GAS ATOMS IN THE INITIAL
C BUBBLE SIZE.

REAL A(1:9),REZ(1:9),IMZ(1:9),TOL,C
REAL AC,BC,RG,GAMMA,PI,R,T,P,V,NATOMS
REAL NATOM(-20:100),DOSE(-20:100),STEP
INTEGER N,IFAIL,R2,R1

PRINT*, 'INPUT THE GAS TYPE'
READ(1,'(A)')GAS
IF(GAS.EQ.'AR') THEN
  DATA AC,BC/O.13625,3.219E-5/
ELSEIF(GAS.EQ.'HE') THEN
  DATA AC,BC/O.003456,2.37E-5/
ELSE
  PRINT*,'ARE YOU SURE? TRY AGAIN'
  GO TO 4
ENDIF
DATA IFAIL/0/,N/4/,PI/3.141592654/
DATA GAMMA,RG/1.9,8.3143/
PRINT*,'INPUT INITIAL BUBBLE RADIUS IN METERS.'
READ*,R

P=2*GAMMA/R
V=4*PI*(R**3)/3
T=300
A(1)=AC*BC
A(2)=-1*AC*V
A(3)=(P*BC+RG*T)*(V**2)
A(4)=-1*P*(V**3)

DO 10 1=1,3
  REZ(I)=0
  IMZ(I)=0
10 CONTINUE

CALL C02AEF(A,N,REZ,IMZ,TOL,IFAIL)
DO 20 1=1,3
  IF(IMZ(I).NE.C.O) GOTO 20
  NATOMS=REZ(I)*6E23
20 CONTINUE

PRINT* ',NUMBER OF GAS ATOMS=',NATOMS
PRINT* ',PVPIR'
PRINT*,P,V,PI,R

C SECONDLY TO CALCULATE THE SIZE OF BUBBLES THEREAFTER
C GROWTH BY GAS ATOM ACCUMULATION+EASY RELAXATION ASSUMED.
NATOMCO)=NATOMS/6E23
PRINT*, 'INPUT YOUR INITIAL DOSE (IONS.CM-2)'
READ*,DOSE(0)
PRINT*, 'INPUT THE DOSE STEP REQUIRED FOR THE CALCULATION'
READ*,STEP
PRINT*, 'INPUT YOUR STEP RANGE; -20,100 PERMITTED'
READ*,R1,R2
DO 30 I=R1,R2
  NATOM(I)=NATOM(0)+(I*STEP*NATOM(0))/DOSE(0)
  DOSE(I)=DOSE(0)+STEP*I
30 CONTINUE
CONTINUE
N=9
IFAIL=0
DO 45 I1=1,9
   REZ(I1)=0
   IMZ(I1)=0
45   CONTINUE
C=4*PI/3
A(1)=-2*GAMMA*(C**3)
A(2)=0
A(3)=RG*T*(C**2)*NATOM(I)
A(4)=2*GAMMA*(C**2)*NATOM(I)*EC
A(5)=0
A(6)=-AC*C*(NATOM(I)**2)
A(7)=0
A(8)=0
A(9)=AC*EC*(NATOM(I)**3)
C   DO 42 I1=1,9
C     PRINT*,A(I1)
C2   CONTINUE
CALL C02AEFC(A,N,REZ,IMZ,TOL,IFAIL)
C   PRINT*,
   DO 46 I1=1,9
   PRINT*,REZ(I1),IMZ(I1)
   IF(IMZ(I1).NE.0) GO TO 46
   IF(REZ(I1).LE.0) GO TO 46
     R=REZ(I1)
   C
   PRINT*,RADIUS,R,GAS ATOMS,NATOM(I)
   WRITE(7,#)DOSE(I)/1.0E16,R*1.0E9
   C
   PRINT*,
   C
   PRINT*,RADIUS,R,DOSE,DOSE(I)
   C
   C6 PRINT*,***************',I',I',I
46   CONTINUE
4C   CONTINUE
   END
PROGRAM ABS

DOUBLE PRECISION CC, CCU, CCUO, AO, ACUO, ACU, D, COSEC, T, IO, ICU, I

DOUBLE PRECISION I1, KCUO, T1, AOCU, I1O, I1CU, TO, COO, ACUZ, DO

DATA CC, CCU, CCUO, AO/0.1273, 0.4098, 0.5073, 3.888/
DATA ACU, D, COSEC, KCUO/103.4, 7.33, 1.662, 0.4055/
DATA ACUO, AOCU/72.7, 121.3/
DATA COO, ACUZ, DO/0.1278, 103.5, 7/

C

PRINT*, 'INPUT OXIDE THICKNESS'
READ*, TO
PRINT*, '***************************************************************************
PRINT*, TO*1E7
WRITE(6,*) TO*1E7
PRINT*, '***************************************************************************
I=0
DO 20 T=1E-6, 200E-7, 1E-6
   IF(T.LE.2*TO)GOTO 10
   I0=COO*(1-EXP(-1*AO*D*COSEC*T))-(1+EXP(-1*AOCU*D*COSEC*(T-TO)))/AO
   ICU=CCU*(1-EXP(-1*ACU*D*COSEC*(T-2*TO)))*(EXP(-1*ACUZ*D*COSEC*(T-TO)))/ACU
   I=KCUO*I0/ICU
   T1=T*1E7
   WRITE(7,*) T1, I1
10 CONTINUE
20 CONTINUE
C30 CONTINUE
END
TO CALCULATE APPROX. WT% AND AT% OF ARGON

REAL CC,KCA,NA,HC,TA,T(100),EXPAT,EXPCT,IA(100),IC(100),EXP1
REAL AA(100),CA(100),CAB(100),EXPAB,AAB(100),DOSE(100)
DATA CC,KCA,NA,HC,TA,0.4098,1.68,1587,103.4,70E-7/

READ(7,4) N
DO 10 I=1,N
READ(7,*)DOSE(I),IA(I),IC(I),T(I)
READ(7,505)IA(I),IC(I)
READ(7,910)T(I)
10 CONTINUE

T12,F5.2,T22,F5.2,
WRITE(1,1000)
WRITE(1,1100)

CALL EXPON(MA,TA,EXP1)
EXPAT=EXP1
DO 20 I=1,K
CALL EXPON(MC,T(I),EXP1)
EXPCT=EXP1
CA(I)=((IA(I)*MA*CC)/(IC(I)*KCA*MC))*(1-EXPCT)/(1-EXPAT)
CALL AT(CA(I),ATOMIC)
AA(I)=ATOMIC

CALL EXPON(MA,T(I)-TA,EXP1)
EXPAB=EXP1
CAB(I)=((IA(I)*MA*CC)/(IC(I)*KCA*MC))*(1-EXPCT)/((1-EXPAT)*EXPAB)
CALL AT(CAB(I),ATOMIC)
AAB(I)=ATOMIC
WRITE(1,1200)DOSE(I),CA(I)*100,AA(I)*100,CAB(I)*100,AAB(I)*100

C PRINT*, 'WEIGHT %'
C PRINT*, 'TOP1',CA(I)*100,'BOTTOM1',CAB(I)*100
C PRINT*, 'ATOMIC %'
C PRINT*, 'TOP',AA(I)*100,'BOTTOM',AAB(I)*100
C PRINT*, '------------------------
20 CONTINUE

C FORMAT(E7.1,I6,I6,E6.0)
C FORMAT(I6,I6)
C FORMAT(E6.0)
1000 FORMAT(T2,' DOSE',T12,'WT%',T22,'AT%',T32,'WT%',T42,'AT%')
1100 FORMAT(T2,'AR- TOP',T22,'AR- TOP',T32,'AR- BOT',T42,'AR- BOT')
1200 FORMAT(T2,E8.2,T12,F5.2,T22,F5.2,T32,F5.2,T42,F5.2)
END

C SUBROUTINE EXPON( M,T1,EXP1 )
REAL D,COSEC,M,T1,EXP1
DATA D,COSEC/7.33,1.662/
EXP1=EXP(-1*M*D*COSEC*T1)
RETURN
END

C SUBROUTINE AT(CAT,ATOMIC)
REAL CAT,NC,WA,WZ
DATA WA,NC,WZ/39.95,63.55,91.22/
ATOMIC=0
ATOMIC = (CAT*(WC+HZ))/(CAT*(WC+HZ-2*WA)+2*WA)
RETURN
END
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