Some Aspects of High Voltage Electron Radiation Damage Studies in Copper Aluminium Alloys

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Preface

This dissertation, no part of which has been submitted for a degree elsewhere, is an account of the work carried out by the author in the Department of Metallurgy and the Science of Materials, Oxford University under the supervision of Dr. M.J. Goringe. Studies by others mentioned in the text are duly acknowledged and an alphabetical list of references is given at the end of the thesis.

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Abstract

Electrons passing through a metal specimen in a H.V.E.M. may displace lattice atoms permanently, depending on the threshold accelerating voltage. While single atomic defects cannot be resolved in the microscope image, defect reactions allow us to detect the damage and to perform in-situ studies during irradiation.

Since the first application by Makin (1968), this method has proved to be particularly successful in studying the formation and growth of defect clusters which become visible in the microscope image after some fifty defects have agglomerated. In many cases, it is then possible to deduce the nature of the agglomerating defect from contrast experiments.

The cluster formation can be studied under a variety of experimental conditions such as electron energy, orientation, electron flux, temperature impurity concentration etc., though it is also necessary to take into account the effects of foil surfaces when comparing H.V.E.M. results with those of reactor experiments.

In this thesis, the results of some experiments which have been performed on thin foils of copper and copper aluminium alloys are presented. The techniques of specimen preparation are discussed in Chapter 2, with special reference to the prevention of gas diffusion into the foil during the electropolish treatment. The defect clusters formed during irradiation were analysed and identified. Chapter 4 discusses the nature of the rhombus perfect loops revealed by using conventional strong beam analysis and also the high resolution 'weak beam' dark field mode. Similar techniques were used in Chapter 3 to understand the nature of Frank loops and the mechanism of unfaulting by the passage of Shockley partials to form perfect loops. The dissociation of the Frank partial dislocation into a stair-rod and a Shockley partial was also studied, by imaging the loops in {113} reflections at the <110> beam direction.

In Chapter 5 the weak beam technique has been applied to the study

of irradiation produced 'elongated' perfect loops and the influence that specimen electropolish temperature and alloy concentrations has on the nucleation of these defects has been discussed. The precautions adopted, in order to obtain reproducible results for loop density measurements are considered in Chapter 6, while Chapter 7 discusses the significance of the Brown, Kelly and Mayer (1969) theory of loop nucleation in understanding the fundamental aspects of radiation damage in copper aluminium alloys. A surface correction factor proposed by Goringe (1971) has been applied, to take into consideration the diffusion of point defects to the foil surfaces. The stereo technique has been used extensively in this thesis to measure the size and depth distributions of loops.

Chapter 8 discusses the effect that H.V.E.M. in-situ annealing treatments prior to irradiation, have on the nature and density of the subsequent damage and a mechanism of short range ordering has been proposed to explain the results. Irradiations performed at high dose rates and temperatures for considerable periods of time revealed that Cu/Al alloys which had <u>not</u> been given an anneal treatment after the electropolish were very resistant to the formation of voids, while those specimens which had the pre-irradiation anneal, nucleated and grew voids as rapidly as in the pure copper specimens. Chapter 9 discusses the significance of the preliminary observations of this effect.

The growth behaviour of interstitial rhombus and Frank loops under constant electron irradiation was traced at several different temperatures for each metal. At elevated temperatures, the Frank loops in copper grew linearly with irradiation time while similar loops in the copper aluminium alloys grew with a time exponent of between .6 and 2.6. These results are illustrated in Chapter 10 and various mechanisms have been suggested to account for the irregular growth.

Chapter 11 contains various conclusions and suggestions for further work.

Introduction

Since electron microscopy involves the exposure of specimens to irradiation by electrons, there is the inherent consequence of radiation damage, which in many cases does not affect observations, but it can happen that such effects produce undesirable changes in the specimen. These phenomena can be exploited in some circumstances for useful purposes.

In conventional microscopes operating at 100 keV, radiation damage is found particularly in biological and other materials, in which ionisation effects arising from the displacements or excitation of electrons are serious. In metals and other good conductors this damage mechanism is ineffective, but important irradiation damage effects arise from atomic displacements, which occur if the microscope operating voltage is sufficiently high.

An energetic electron passing through a solid, collides with the atomic nuclei and transfers kinetic energy to them, with an efficiency depending on the atomic weight of the metal. If the energy transferred to an atom is sufficient, it will be displaced from it's site in the crystal lattice, to become an interstitial, leaving behind, a vacancy. The ultimate form of damage depends upon the behaviour of these point defects.

The observation of defect clusters in neutron irradiated aluminium and copper by Silcox (1959 and 1960) initially focussed attention upon irradiation damage in nuclear reactors and the resulting microstructural modifications. The radiation hardening of reactor materials by these clusters was a primary concern in the design of the early generations of reactors Makin (1966). However, as reactors progressed to higher neutron fluences and temperatures, a second type of defect caused by irradiation damage was observed, the void Cawthorne (1967). As a consequence of this void formation, irradiated materials undergo a volume expansion or swelling. For this behaviour and possible embrittlement by voids, the problem of void formation has become a primary concern in the choice of materials

tor new generations of reactors. The swelling problem is especially significant in the proposed fast breeder designs where high damage rates and elevated temperatures enhance the formation of voids in reactor elements. At the present time, virtually all metals and a variety of non metals have been shown to undergo swelling during irradiation at appropriate temperatures $\simeq .3\ T_m - .55\ T_m$ Norris (1972).

Some of the materials to be used in future nuclear reactors must be able to withstand a hostile neutron environment for periods up to thirty years. Since the microstructure of the materials and their physical and mechanical properties change markedly on exposure to high neutron fluences, it is desirable to predict and control these changes. As long term material tests of up to thirty years are not feasible, great interest centres on accelerated tests.

The field of radiation studies has applications throughout fission and fusion reactor technology as well as in space technology. Deficiencies in understanding the changes induced by radiation in materials used in reactors have led to costly modifications in design and operational procedures. Lack of complete knowledge of the complex processes in engineering materials requires periodic retrieval of samples from present light water reactors for material testing; in some cases it causes operation at lower power than the design intended and leads to a need for more auxiliary equipment. There is also the possibility that the deterioration of the containing vessels may make it necessary to shut down the reactor and shorten its life. Zebroski (1975) estimated that the economic cost of these deficiencies in knowledge at about US $480 million in 1974, with an increase to over US $1 billion in 1982.

The displacement damage in electron irradiated metals has many similarities to other types of irradiation and studies in general have flourished due to their pure scientific interest and also to the technological demands of the nuclear power industry. Damage studies often employ

neutron irradiation over short periods in a reactor, or in laboratory experiments heavy ion irradiation can be provided in an accelerator. In both of these cases, major effects are due, as with electron irradiation, to atomic displacements but there are, in addition, other processes such as the introduction of impurities either by nuclear transmutation or by the bombarding ions stopping within the specimen. Electron irradiation has fewer complications and is consequently an excellent means of studying the fundamentals of displacement damage in that the H.V.E.M. can be used as a low cost rapid screening test for new alloy development.

High energy electron irradiation produces a simple type of damage and allows the separation of the importance of displacement and thermal spikes from the effects of the induced defect supersaturation. In addition, the H.V.E.M. allows continuous monitoring of the defect structure as a function of displacement dose. Such observation permits the investigation of the formation of the two types of irradiation damage, dislocation loops and voids. The inter-relations between the formation of these two defects can be examined. On the other hand, there are several limitations placed on irradiation damage studies, several of which are reflections of the interaction of the foil surfaces with the induced defects. These are capable of masking the bulk material irradiation behaviour.

Irradiations were performed on thin foils of copper and copper aluminium alloys; copper being chosen because of the large amount of information in the literature in this material produced by neutron, ion and electron irradiation. Copper aluminium alloys were investigated on the basis that the stacking fault energy of this metal has been determined Ray (1971).

Defect Production

The irradiation damage process can be divided into two contributing factors; the defect production and subsequent clustering processes. The manner of defect production can affect the type and concentration of

defects produced and their spatial distributions which will affect the clustering process. The initial step of the defect production process is the collision between the lattice atom and the bombarding species. The type of bombarding species and the type of interaction between it and the lattice atom determine the nature of the collision, and the cross section. The energy transferred to the lattice atom is determined by its mass and the effective mass of the bombarding particle and its incident energy. In the case of electron irradiation, the interaction with the lattice atom is a direct Coulombic attraction with the nucleus of the target atom. Displacement damage can be caused in a variety of materials by electrons of energies ranging from .2 - 1.5 MeV. Relativistic corrections of the effective mass of electrons of these energies must be used in describing their motion. As a result of the large mass of the lattice atom relative to the electron, the collision affects only the momentum of the electron, but not its energy.

Consider an elastic collision between an electron (rest mass m_o, kinetic energy E_1) and an atom of mass m_2 at rest. The momentum and kinetic energy of an electron with rest mass m_o and velocity U_1 are

$P_1 = mU_1$

with $$m = \frac{m_o}{\sqrt{1 - \beta^2}}$$

where $\beta = \frac{U_1}{C}$ and $E_1 = (m - m_o)C^2$.

The momentum transfer in a collision with scattering angle θ_1 $\Delta p = 2mU_1 \sin(\theta 1/2)$ and the corresponding energy transfer given by $\frac{(\Delta p)^2}{2m_2}$ is then

$$E_2 = \frac{2m^2 U_1^2 \sin^2(\frac{\theta_1}{2})}{m_2}$$

which transforms to

$$E_2 = \frac{2E_1(E_1 + 2m_oC^2)\sin^2(\frac{\theta_1}{2})}{m_2C^2}$$

and whose maximum possible recoil energy $\bar{E}_2$ is given when $\theta_1 = \pi$ by

$$\bar{E}_2 = \frac{2E_1(E_1 + 2m_oc^2)}{m_2c^2}$$

A crude but useful assumption for establishing the criterion for a displacement to occur, is that the atom is bound to its site in the lattice in an isotropic square well potential of depth E_d. This threshold represents the minimum energy required to create the Frenkel pair and to move the self-interstitial a distance from its vacancy sufficient to prevent spontaneous recombination. Thus any energy transfer less than E_d does not create a defect, while any greater has a unit probability of doing so, there being a single step threshold. However, the larger portion of the threshold energy arises from the rapid motion of the ejected self-interstitial through the lattice. As it passes through the relatively dense lattice, the interstitial collides with many stationary atoms, losing a portion of its kinetic energy to each atom. The number of atoms that the interstitial strikes along its path determines the distance it travels. This is the partial origin of the orientation dependence of the threshold energy. Along different crystallographic directions, the lineal density of atoms with which the interstitial will collide varies. The values of threshold voltage for cluster formation in copper has been measured by Kenick and Mitchell (1975) to be 525 keV <100>, 380 keV <110> and 550 keV <111>. It is possible however for displacements to occur at energies below the threshold for bulk irradiations, when the lattice periodicity is slightly disturbed due to the presence of dislocations, impurity atoms, grain boundaries and similar extended defects which distort the lattice regularity. Light impurities can also produce sub-threshold knock-ons, because the energy transferred to a lattice atom can be increased by a series collision, in which a lighter impurity atom acts as an intermediate. Generally, the interstitial impurities, hydrogen, carbon, nitrogen and oxygen are prime

considerations in this mechanism.

The second important parameter in the displacement process is the cross section for the displacement of an atom, which gives the probability of an atom being displaced by an electron of a particular energy. This cross section is determined by the scattering cross section of the atom for an electron of that energy and the magnitude of the energy transferred to the atom relative to the threshold energy. Since both of these quantities exhibit some angular dependencies, the displacement cross section represents an integral over all possible collision angles.

Mott (1929) (1932) treated the scattering of an electron by a point nucleus by Dirac electron theory; essentially relativistic quantum theory. However, the exact scattering equation is an infinite series expansion, which does not have an analytic solution. Several authors have made approximations to the solution for the scattering cross-section, the most widely used is that presented by McKinley and Feshbach (1948)

$$\sigma = \frac{\pi z^2 e^4 (1-\beta^2)}{m^2 c^2 \beta^4}\left[\frac{E_2}{E_d} + 2\pi\alpha\beta\left(\frac{E_2}{E_d}\right)^{\frac{1}{2}} - (\beta^2+\pi\alpha\beta)\ln\frac{E_2}{E_d} - (1+2\pi\alpha\beta)\right]$$

It has been pointed out by Seitz and Koehler (1956) that the McKinley-Feshbach cross-section should be sufficiently accurate for light elements. However, for the heavier elements the more exact Mott series solution is required. Oen (1965) performed the numerical solution using this series for a variety of elements and electron energies. The cross-sections were compared with those calculated using the McKinley-Feshbach equation and found to be within 15% for all elements below z = 31. These displacement cross-sections for copper are tabulated in Fig. 1/1.

The concentration of displacements produced, and of point defect pairs created per second, is given by the displacement rate

$$K = \phi\sigma$$

where ϕ = electron flux. The displacement damage rate after time t is $\phi\sigma t$ usually quoted in displacements per atom.

It is possible for one electron-atom collision to result in more than one point defect pair, if the primary knock-on, the struck atom, is given sufficient energy to produce further displacements via atom-atom collisions. For $E_2 >> E_d$, such secondary displacements become very numerous and their calculation requires various considerations. If the energy transmitted to the atom is greater than twice the displacement energy then the displaced atom may in turn displace other atoms. This process may be taken into account by multiplying the cross-section by an averaged factor N Makin (1968) given by;

$$N = 1 + \ln \left(\frac{E_2}{2E_d}\right)$$

where $E_2 > 2E_d$.

These secondaries have been dealt with in the displacement cross-section calculations, which are included in Fig. 1/1. In this thesis, a cross-section of 75 barns was used in all the irradiation dose rate calculations. Though there is considerable ambiguity in this value, the results will be self-consistent, since the same irradiation beam direction of <532> was used throughout, unless otherwise specified.

The primary knock-on dissipates its energy by electronic excitation and by collisions with other atoms in which secondary knock-ons are produced, until eventually it comes to rest as an interstitial. In irradiations with neutrons in a nuclear reactor, each primary collision produces many secondary knock-ons; this is also true of irradiation with ions of a few keV or more, whereas in the case of irradiation with electrons of 1 MeV or less, only one or two vacancies and interstitials are produced by each primary collision. Since the probability of hitting another atom increases as the primary knock-on loses its energy, it travels shorter and shorter distances between the production of vacancies. This results in a very high concentration of vacancies near the end of the primary knock-on path, with the interstitials (secondary knock-ons) moving out of the vicinity

and dissipating their energy as heat. The zone of high vacancy concentration and temperature which is produced, is called a displacement spike and it may result in the nucleation of a small void or vacancy type dislocation loop. Although the spatial distribution of lattice defects differs for these three types of irradiation (e.g. displacement spikes are produced only by ions or neutrons and the penetration depth or ions and electrons is quite small), they all result in concentrations of interstitials and vacancies which are well above the thermal equilibrium concentrations. The supersaturation of these lattice defects provides the driving force for the nucleation of voids and dislocation loops, both of which have been observed as a result of irradiation by each of the three irradiations discussed. Since ion irradiation and electron irradiation in the H.V.E.M. are capable of producing an average defect supersaturation several orders of magnitude greater than that obtainable in nuclear reactors, these methods have been extensively used to investigate the probable effects of long term irradiations in nuclear reactors.

The typical shape of a fully focussed beam in the microscope is approximately gaussian and the maximum flux densities in presently available high voltage electron microscopes are in the range 10^{17} - 10^{21} el/cm^2/sec, giving a damage production rate of between three and six orders of magnitude greater than in a conventional accelerator. The beam current may easily be reduced from these maxima either by reducing the total current while keeping the same profile or by defocussing the condenser lenses so as to produce a more uniform larger illuminated area. However, limits on these values are set by the heating effect of the electron beam on the one hand and the ability to observe and record micrographs over a short period of time.

Point Defects and Defect Clustering

In the absence of irradiation and in thermal equilibrium, the fractional concentration of vacancies C_V at a temperature T is given by

$$C_V = \exp \frac{S_V^F}{k} \exp - \frac{E_V^F}{kT}$$

where k = Boltzmann's constant

S_V^F = formation entropy

E_V^F = formation energy.

A corresponding expression applies to interstitials. A key difference between the vacancy and the interstitial is that the latter produces severe strains in the surrounding lattice with the consequence $E_I^F > E_V^F$. Typical values are $E_I^F = 4$ eV, $E_V^F = 1$ eV, $T = 1000^oK$ and an entropy factor of unity give $C_I \simeq 10^{-20}$, $C_V \simeq 10^{-5}$. Thus interstitials in thermal equilibrium can usually be ignored, whereas vacancy concentrations become very significant at high temperatures.

A point defect migrates from one lattice site to another, or from one interstitial site to another, when the potential barrier separating the two sites is overcome by the thermal fluctuations in the crystal. The atoms have a natural vibration frequency ν_o and assuming Maxwell-Boltzmann statistics, the jump frequency over the barrier is given by:-

$$\nu_v = \nu_o \exp \frac{S_V^m}{k} \exp - \frac{E_V^m}{kT}$$

where S_V^m is the migration entropy and E_V^m is the migration energy. The interstitial jump frequency ν_I is given by a similar expression. A defect moves through the lattice until it becomes trapped at a region of lower potential, examples of such sinks being

(1) mutual annihilation of point defects with opposite sign,

(2) annihilation at the foil surfaces,

(3) interaction with impurity atoms,

(4) agglomeration of defects of the same type forming defect clusters such as dislocation loops, stacking fault tetrahedra and voids,

(5) defect absorption at internal sinks such as grain boundaries, dislocations and other lattice defects.

There are many techniques for studying vacancies, since these are detectable in thermal equilibrium or in quenching experiments. Self diffusion in metals usually occurs by a vacancy mechanism and its activation energy may be interpreted as the sum $E_V^F + E_V^m$. Seeger et al. (1970) quote some vacancy parameters for various metals, but the actual values are hotly disputed. There is even less understanding of interstitials, which can only be studied by irradiation experiments. Theoretical calculations by Johnson (1962) suggest that in copper $E_I^F \simeq 4$ eV and $E_I^m \simeq .1$ eV. Thus interstitials are very much more mobile than vacancies. An important category of experiments employs electron irradiation at liquid helium temperatures, the defects created then being practically immobile. During a subsequent anneal at gradually increasing temperatures, various defect processes are activated by thermal energy at different stages, it being possible to detect them by resistivity measurements. The interpretation of these experiments is however controversial.

Self interstitials are mobile in most metals at temperatures above 100 - 150^{o}K. Vacancies, on the other hand do not become mobile until temperatures approximating ambient are reached. Divacancies in general are considered to have intermediate mobility with respect to self-interstitials and vacancies. For clustering of the point defects, a finite number of defects must survive both recombination and trapping at sinks. During the displacement process, some fraction of the Frenkel pairs produced are close pairs, where the vacancy and self-interstitial are separated by a small distance and there is some finite binding energy between the two defects. If there is some mobility to either or both defects, they will be attracted and will undergo correlated recombination. In face centred cubic metals, such correlated recombination of close pairs is associated with annealing stages 1a - 1c. Schilling et al. (1970), Iselar et al. (1967). Non close pairs can annihilate by uncorrelated recombination. Since the self interstitial in such a pair is still closest to its own vacancy, there is a

finite probability that it will recombine rather than cluster. This process is associated with the ld annealing stage in f.c.c. metals. Free migration of the interstitial is associated with stage le, at about 50°K. Between ≃70°K and 220°K (stage 2), annealing is highly impurity dependent and it is supposed that interstitials previously trapped at solute atoms are now being released. Stage 3 between 220°K and ≃300°K is attributable in one interpretation to vacancy migration, but is an alternative scheme to a second form of interstitial. Stage 4 between 300°K and 450°K then becomes according to the first school of thought the release of vacancies from traps and according to the second, the free migration of vacancies. Experiments performed in this thesis have been carried out at temperatures in the range 300°K - 600°K and tentative conclusions have been drawn about defect mobilities from the observed activation energies.

If the point defects are sufficiently mobile to cluster, the next concern is the stable configuration of the resulting extended defects. For interstitial clusters, the stable form is a dislocation loop, either faulted or perfect depending on the size of the loop. For smaller loops, the Burger's vector of the faulted loop reduces the self-energy of the dislocation. For larger size loops, the removal of the stacking fault and its associated energy favours the perfect loop. Since the transformation from faulted to perfect loop is possible by the passage of a second partial dislocation across the fault, the normal sequence for interstitial cluster is initial growth as a faulted loop, unfaulting above some critical size and subsequent growth as a perfect loop Makin (1970), Norris (1970) Urban (1971). The interstitial analogues of the stacking fault tetrahedron and the void are energetically unfavourable and have not been reported.

In the case of vacancy clusters, the situation is slightly more complex as a reflection of the addition of other possible stable configurations. Aside from the faulted and perfect loops, vacancies can cluster as a vacancy disc or uncollapsed dislocation loop, a stacking fault tetrahedron or a

void. Computer calculations have shown that the tetravacancy in f.c.c. metals may form either as a tetrahedron the precursor of a stacking fault tetrahedron or void, or as a planar rhombic cluster, the precursor to the faulted loop Wenzl (1970). The vacancy tetrahedron is metastable relative to the rhombic form, but may be stabilized by gas atoms. Both computer calculations and energy balance computations indicate that the uncollapsed vacancy disc is unstable relative to the faulted loop for clusters containing more than 4 - 10 vacancies. Through arguments similar to that used for interstitial clusters, it can be shown that the stable dislocation configuration for vacancy type defects is the stacking fault tetrahedron for small sizes, the faulted loops for intermediate sizes and the perfect loops for large defects. Stacking fault tetrahedra have been observed primarily in damaged noble metals, Wilkens (1970). Since there are dislocation reactions which can transform one of these forms to the other types, a possible growth sequence is tetrahedron, faulted loop and finally perfect loop.

Since there is no transformation between a vacancy dislocation loop and a void, the defect type which is nucleated will be the defect observed throughout the irradiation. Calculations of relative energies indicate that, since the interfacial energy is significantly greater than the stacking fault energy, the dislocation loop is the energetically favoured defect form. However, the majority of irradiation damage studies report the presence of voids, and it is generally accepted that gas atoms stabilize the void nucleus relative to that of the dislocation loop. By the addition of the pressure-volume energy term, the gas atoms prevent the collapse of the vacancy cluster to a dislocation loop. After the cluster grows to a size of 10 - 20 vacancies, it can be considered a void and is unable to transform to a loop and will continue to grow as a void. In neutron irradiated metals small vacancy loops are observed, but do not seem to grow with continued irradiation, Makin (1963). It is generally believed that these

vacancy dislocation loops are produced in the depleted zone of a displacement cascade. Despite being the stable defect cluster under normal conditions, the vacancy loop becomes dynamically unstable in the presence of supersaturations of both vacancies and interstitials. As a result of the higher hydrostatic stress-field of the interstitials, the interaction energy between the interstitial and the dislocation is greater than that between the vacancy and the dislocation. Thus there is a net flux of self-interstitials to a dislocation loop, irrespective of its character. A vacancy loop, even if generated in a displacement cascade, cannot grow in an irradiation environment and in general will shrink and disappear.

The majority of irradiation damage studies are concerned with void formation and the associated swelling and volume expansion. However, most of results illustrated in this thesis relate to the radiation damage stage prior to void formation. The main aims of this thesis are:-

(1) To determine the effect of alloy concentration on the loop densities, nature and growth.

(2) To compare the experimental loop density results with those of currently acceptable theories after taking into account the effects of the foil surfaces.

(3) To analyse the structure of the loops using high resolution 'weak beam microscopy'.

(4) To determine the effect of specimen microstructure e.g. gases, short range order etc. on the form of the subsequent loop and void damage.

CHAPTER 2

Specimen Preparation

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2.1 Crystal Preparation

Copper and homogenised copper-aluminium ingots of nominal composition 2,5,7,10 and 16 atomic percent were obtained from Johnson-Matthey Co., swaged to size, placed in a carefully ground graphite mould and grown into crystals of dimensions 1 cm. diameter x 10 cm. in length using the Bridgeman technique.

In the course of experiments carried out for this thesis, two sets of single crystals were grown; the first at a pulling rate of 2.2 cm/hr and the second at a rate of 3 mm/hr. The crystal growth rate was reduced, when it was realised that thin foils cut from fast grown crystals were difficult to polish and did not give reproducible results after electron irradiation. The differences in the resultant crystal characteristics have not been investigated.

The crystals were carefully removed from the moulds, cleaned in nitric acid and then etched in a solution of concentrated hydrochloric acid saturated with ferric chloride. The crystals were then x-rayed at several positions along their length and those judged to be free of imperfections were placed in a vacuum furnace at $\simeq 10^{-5}$ mm.Hg. for a 24 hour anneal at 1000°C.

After slow cooling to room temperature, the crystal was mounted on a goniometer and orientated for <111> foil normal slices using back reflection Laue x-ray photographs. After two cm. from each end of the crystal was cut off and discarded, the remaining rod was cut into slices .6 mm. in thickness using the 'Servomet' spark cutter operating on range 5. Since spark erosion produces dislocation damage near the cut surface of the specimen Hazzledine (1966), a compromise of spark intensity, cutting time and slice thickness was required. It was found that range 5 and $\simeq$.6 mm. thick slices produced specimens with no observable cutting damage.

The excess specimen thickness was removed by chemical erosion using a solution of 80% Nitric acid, 20% water with 2 gms. of nickel chloride per 100 cc. of solution. The nickel chloride was added to reduce pitting of the specimen surfaces. The surfaces of the sectioned slices were

planed and polished using chemical cloth polishing. The markings on the surface and the grooves produced by the spark cutter were first removed using the method proposed by Mitchell (1967), which involved stretching tightly a piece of cotton sheet over a 9 x 3 x $\frac{1}{4}$" piece of teflon and wetting with a solution of anhydrous cupric chloride in concentrated hydrochloric acid. The smoothing and polishing operation was carried out in a fume cupboard, the hands being protected by surgical gloves. The slice was then moved gently backwards and forwards over the acid cloth. Since the initial smoothing operation produced slightly undulating highly polished surfaces a second cloth polish in a different solution was used to produce optically planar slices. This solution consisted of:

200 ml. orthophosphoric acid

200 ml. glacial acetic acid

200 ml. concentrated hydrochloric acid

15 ml. concentrated hydrochloric acid saturated with anhydrous cupric chloride

5 ml. polyethylene glycol 400.

These techniques have been adopted, to remove irregularities of the specimen surface so that accurate electropolish conditions can be achieved. A further advantage in having optically planar surfaces, is that flaws will not be able to contribute to irregular jetted profiles and this is especially important at low temperatures ($-75^{\circ}C$) when electropolishing of thin foils can take as much as 2 hours. Slices thinned using the cloth polish were stuck on to brass blocks using a mixture of 'silverdag' and glue. 2.3 mm. and 3 mm. discs, suitable for electron microscope use were trepanned from the bulk slice using the spark erosion technique. The discs were then immersed in acetone to remove all traces of silverdag, glue and grease; washed in water and alcohol, then given a further anneal at $1000^{\circ}C$ for 8 hours, at a pressure of 10^{-5} mm.Hg.

2.2 Initial Thinning of Specimen

The discs were dimpled on both sides using a conventional 'jetting' polish unit with an aqueous solution of 33% orthophosphoric acid, the

current having been adjusted to produce a flat bottomed concave dish. The cross section profile of jetted specimens can be observed by using a stereomicroscope and depends on several variables:-

(a) Jet diameter. An increase in this parameter causes the area of the central flat region to increase, the rate of polish to decrease and the profile to become irregular at the edges due to the increased area of the electrolyte and its turbulence.

(b) Electrolyte velocity. An increase in the head of the solution causes the velocity to increase. At low flow rates oxygen bubbles accumulate, while at very high rates the specimen etches. At intermediate velocities the bubbles are swept away and the polish rate becomes uniform.

(c) Specimen to cathode distance. If the distance between the jet and specimen is increased, the polish area increases and the central plateau decreases in depth but becomes flatter.

(d) Concentration of jetting solution.

(e) Thickness of glass capillary.

These variables were optimized by experiment and by suitable choice of polishing current to give the profile shown in fig. 2/1(d). In order to obtain consistent cutting rates the discs must have imperfection free parallel planar surfaces and have the concave dishes accurately aligned. Once the variables have been set, they must be kept constant as each specimen is polished otherwise the polishing conditions will change. The main influence on the variability of specimen removal rate was found to be the electrolyte temperature, which can increase by several degrees, depending on the distance between the specimen and the nozzle. Fig. 2/2 illustrates the effect that a small rise in temperature has on the polishing rate for a copper foil. Since the temperature of the electrolyte was observed to vary between 15^{o} and 25^{o}, it had to be cooled by passage through an ice bath on the return line to the reservoir. With the aid of graphs similar to fig. 2/2 for each alloy accurate determinations

of the specimen removal rate were made. Specimens were not jetted more than 2 hours prior to insertion into the microscope in order to prevent the build-up of deposits on the surface, which could not be removed by the final electropolish treatment. The electrolyte was also changed every two weeks in order to prevent contamination by the copper removed from the foil surfaces.

2.3 Final Electropolish

The final polish was carried out immediately before inserting the specimen in the microscope. It had two functions:- to provide a sufficiently slow thinning rate to make it possible to stop polishing the instant breakthrough occurred, and to give the final surface an electron-optically smooth finish free from oxide layers. Control of the polishing rate was originally exercised by pouring liquid nitrogen onto the electrolyte surface in order to cool it down. However, this method does have the following disadvantages:-

(1) Solid layers of ice form on the electrolyte surface.

(2) Numerous bubbles form throughout the solution, which attach themselves to the specimen.

(3) Large temperature gradients formed in the solution.

Solutions were always mixed just prior to the final polish, since it was found that solutions stored for a considerable time gave rise to adverse polishing results. A further disadvantage of this method of polishing is that chemical reactions can cause the specimen temperature to rise by as much as 40°C, with the result that the final electropolish becomes uncontrollable.

Experiments revealed, that specimens having clean surfaces, large thin areas and free from bends were best achieved by electropolishing at very low temperatures and to achieve these conditions the apparatus of fig. 2/3 was constructed. This device consisted of a double walled glass beaker of volume 500 cc. with an optical window and a device for

pumping nitrogen gas between the walls, to act as a coolant. In addition to eliminating bubbles in solution, it prevented the formation of water vapour inside the beaker and allowed an accurately controlled temperature ($\pm 2^{o}C$) to be obtained down to the lowest temperatures used ($-80^{o}C$). The optical window ensured that the specimen could be clearly observed without distortion, while the magnetic stirrer performed the double function of promoting a uniform electrolyte temperature and removing any bubbles which evolved from the tweezers.

The discs were held between lacquered platinum tipped tweezers with the ends finely pointed as shown in fig. 2/1(e) rather than the conventional method fig. 2/1(f), since a better viscous layer was established. A small magnet was used to hold the tweezers in the solution facilitating quick and easy removal of the foil without switching off the current. This method enabled specimens to be obtained free from bending or etching effects. The specimens were carefully inserted successively into several beakers of methanol, distilled water and ethanol, but agitation was kept to a minimum. After drying on blotting paper the specimens were handled only by vacuum tweezers and inserted quickly into the H.V.E.M. to prevent the build-up of a thick oxide layer on the surface since this can affect the structure of the subsequent radiation damage.

The solutions that were tried by the author for the polish of copper alloys are:-

(1) D2 solution. 250 cc. orthophosphoric acid
250 cc. ethanol
500 cc. distilled water
50 cc. n-propanol
5 gms. urea at room temperature

(2) 350 cc. orthophosphoric acid
100 cc. orthophosphoric acid saturated in copper phosphate
450 cc. distilled water cooled to $-10^{o}C$.

(3) 33% Nitric acid

67% Methanol cooled to below -40°C

(4) 50% orthophosphoric acid

50% distilled water at room temperature.

At low temperatures, the nitric acid, methanol solution was found to give the best results.

There is some question as to the possible addition of impurities, either hydrogen or oxygen to the foil during electropolishing and the subsequent effect of these impurities on irradiation damage. A two fold approach was undertaken to investigate this possibility in the present study. First, polished foils were heated to 750°C and held for 8 hours and also 20 hours under a dynamic pressure of $\simeq 5 \times 10^{-9}$ torr. in order to outgas such impurities. The second approach was to electropolish discs at a series of temperatures between 0°C and -80°C and to observe the subsequent effect on the radiation damage. Comparison of the damage in foils polished at -35°C with foils polished at -80°C indicated the importance of impurities introduced during electropolishing.

At temperatures of -70°C the final electropolish rate was found to be ≃700 times slower than the jetting rate. An error of 5 seconds introduced when jetting (caused by electrolyte temperature rises, inadequately centred discs etc.) tends to increase the time of final polish to well over one hour. This indicates the necessity for refined polishing techniques, when preparing foils for irradiation in the H.V.E.M.

CHAPTER 3

Analysis of Frank Loops Grown in the H.V.E.M.

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3.1 Burger's Vector Convention

A convenient representation for the sequential ordering of partials and of assigning loop Burgers vectors has been proposed by Thompson (1953). By joining atoms together in a one eighth unit cell by straight lines, one forms the tetrahedron shown in fig. 3/1(a). The inner and outer faces of the tetrahedron represent the four possible {111} glide planes and the edges of the tetrahedron correspond to the six <110> glide directions of the F.C.C. structure. The atom at the origin is labelled D and the other atoms are labelled A, B and C. The mid-points of the faces opposite A, B, C and D are labelled α, β, γ and δ corresponding to the $(\bar{1}1\bar{1})$, $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$ and (111) planes. If the tetrahedron is opened out from point D, the planar arrangement is shown in fig. 3/1(b). The {111} planes are presented by Greek letters and the perfect dislocations by Roman letters.

The convention adopted in this thesis for defining an intrinsic stacking fault arrangement is that on viewing a perfect dislocation along the positive sense of the line, the Greek-Roman partial e.g. $\overline{\delta B}$ is on the left and the Roman-Greek partial e.g. $\overline{A\delta}$ is on the right, viewed from outside the tetrahedron.

The conventions used in orienting the tetrahedron are shown in fig. 3/2. There are four possible ways of orienting the tetrahedron as shown in (a), (b), (c) and (d) of which (a) and (c), with the apex (d) into the plane of the paper, has been chosen in this thesis. The ambiguity in the crystal orientation was resolved by noting the position of the <112> and <110> poles in the Kikuchi pattern. When this was known, the tetrahedron (a) or (c) was aligned parallel to the particular diffraction vector chosen. In this thesis, all micrographs were printed emulsion side up, showing the view from above the specimen. The diffraction vectors were then marked on the print, taking into account the lens rotations and the 180° inversion. In order to correctly identify the

loop nature, the (g.b)s inside-outside contrast mechanism Hirsch et al. (1965) was used, with the FS RH convention for labelling the Burger's vector. The various configurations are shown in fig. 3/3. In the convention used here interstitial loops have the Burger's vector as the outward drawn normal if the apex of the tetrahedron is downwards (i.e. if the upward drawn normal to the foil is [111]). For the diffraction vector $\bar{g}$ labelled as shown, the conditions for contrast from an interstitial loop is that $(\bar{g}.\bar{b})s > 0$ and $\bar{n}.\bar{b} > 0$ (where $\bar{n}$ = loop plane normal). For the sense of $\bar{g}$ and s as shown, the local bending of the lattice planes near the image point A is shown by the arrows: in the sense required to move the reciprocal lattice points towards the reflecting sphere to give inside contrast.

3.2 Introduction

As a result of the supersaturation of both self-interstitials and vacancies induced by electron irradiation, these point defects cluster and precipitate in various complex defect forms. The interstitials cluster as dislocation loops, either faulted or perfect, while the vacancies precipitate as voids under most irradiation conditions. As a result of the higher interstitial mobility and the requirement of dislocation biasing for void formation, interstitial loops will nucleate initially. After the dislocation density has achieved a value which provides sufficient biasing, voids are nucleated and grow to observable sizes. Since the study of voids has become in recent years of technological significance, the study of the loops preceding the void formation stage is also of interest.

The sessile loop consists of a layer of interstitials on the {111} planes which have collapsed to form a dislocation loop having a $a/3[111]$ Burger's vector surrounding a region of extrinsic stacking fault. This fault can be eliminated by the nucleation of two Shockley partials (one above and one below the extra plane) by the reaction Barnes (1961)

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

Hirsch (1962) observed small faulted interstitial loops in proton irradiated copper and Mazey (1966, 1968) completed the geometric analysis of single and double faulted sessile loops formed in thin films of copper during proton irradiation at high temperatures. Large faulted loops have also been observed in most metals over the last 15 years by quenching; in particular Clarebrough (1969) formed Frank loops in copper aluminium alloys, by quenching in a carbon monoxide atmosphere. More recently the advent of the high voltage microscope has allowed large interstitial loops to grow in thin foils under dynamic conditions. Sessile loops 1 micron in diameter were grown in copper at temperatures of about 250°C by Makin (1968), Ipohorski (1969), Kiritani (1975) and in Nickel by Norris (1970) and Urban (1971).

The interest in Frank loops has, for this thesis, been stimulated by the fact that many metals allowing Frank loop growth also allow the easy nucleation and growth of voids. Those metals which readily form perfect loops on irradiation appear to be more resistant to void formation, as observed in this thesis, for Cu/Al alloys.

Observations of Frank loops in the H.V.E.M. were carried out on copper, copper .077% aluminium, Cu .15% Al, Cu .31% Al, Cu .98% Al and Cu 2% Al using slow grown crystals. In the higher alloys of Cu 5% Al, Cu 7% Al, Cu 10% Al and Cu 16% Al (all atomic percent) sessile loops only formed under the special conditions of either irradiating fast grown crystals, or annealing electropolished foils cut from slow grown crystals in the microscope at temperatures of ≃550°C, and then irradiating at lower temperatures. Irradiation between room temperature and 300°C showed a damage structure consisting of small point defect clusters which exhibited the characteristic black-white contrast associated with Frank loops ($\bar{l}$ parallel to $\bar{b}$ or the projection of $\bar{b}$ on the image plane). Continuous

Irradiation at temperatures of 250°C produced large faulted loops of a sufficiently low density that easy analysis could be carried out. These loops lie on the {111} tetrahedral planes, are polygonal in shape and exhibit stacking fault contrast fringes within the loop.

Contrary to other experimental evidence (Makin, Norris, Spring, Mazey etc.), it has been found that the loop side directions of growing loops are not restricted to <110> but may align themselves along various other low index directions. Indeed the main characteristic of growing loops in very low stacking fault energy metals, is the very irregularity of the growth process. In the very dilute alloys, 'petal' shaped loops sometimes developed, though this formation generally occurred when the loops were large. At all temperatures the faulted loops were seen to interact and unfault, or unfault spontaneously because of stress. The resultant perfect loops did not rotate to {110} planes, but either remained on the {111} planes, or tried to rotate, ending up in an intermediate configuration between {111} and {110}. This is in contrast also to the loop rotation observed when rhombus loops adopt an equilibrium position near {320} between {110} and {001} reported in Chapter 4.

3.3 Stacking Fault Analysis of Frank Loops

Stacking fault fringes result from the interference between diffracted and transmitted waves by a perfect crystal above and below the fault plane; the stacking fault effectively shifting the lower part of the crystal relative to the fixed upper part by the shear vector $\bar{R}$ of the fault. The corresponding phase angle $\alpha = 2\pi\bar{g}.\bar{R}$, where $\bar{g}$ = the diffraction vector and α is the phase shift of waves diffracted from above and below the fault. The theories of Whelan (1957), Howie (1960) and Hirsch (1965) predict that fringe contrast should vanish when $\alpha = 2n\pi$.

In the experiments carried out, fault contrast in the loops disappeared when <220> or <113> lattice reflections were used. Fig. 3/4 illustrates fault contrast in loops on four different {111} planes using $\bar{g}$ = <111> and

<220>. These loops have been identified as lying on {111} planes, since the loop sides lie along <110> and only {111} planes can contain three <110> sides. Four different {111} planes can be observed when $g = [\bar{1}1\bar{1}]$ as in (d). The foil was then tilted to near [111], where the {220} reflections were imaged. The values of $\alpha = 2\pi\bar{g}.\bar{R}$ for all the loop planes using $g = [\bar{2}20]$ and $g = [\bar{1}1\bar{1}]$ are shown in Table 1(a). The fault contrast vanishes for loops A and B, but not loops C and D. Theoretically, loop D in the $[\bar{1}1\bar{1}]$ reflection shows no fault contrast, but this cannot be observed since it is in the edge on position. If $g = [\bar{2}20]$ and the loop fault vector is either $\bar{R} = \frac{a}{3}[111]$ or $\bar{R} = \frac{a}{3}[1\bar{1}1]$, $\alpha = 0$ for loops A and B, which predicts the vanishing contrast. In the same reflection, fault contrast is visible for loops C and D and $\alpha = \pm \frac{8\pi}{3}$, which predicts visibility of contrast within these loops. For the loops A, B and C where the stacking fault should be visible, $g = [\bar{1}1\bar{1}]$ gives $\alpha = \pm \frac{2\pi}{3}$ in agreement with observation.

3.4 Loop Burger's Vector

The Burger's vector of the faulted loops were established from the diffraction vectors in which the loops vanished, for the Burger's vectors lie in these reflecting planes. The vanishing conditions occur when $\bar{g}.\bar{b} = 0$ Hirsch et al. (1965). The Burgers vector determination of the loops in fig. 3/4 is shown in Table 1(b). The faulted loops on the A, B, C and D planes have been imaged in the Bragg reflections indicated. Considering loop A for example, the Frank partial is out of contrast in all three <220> reflections. Since $\bar{b} = \pm (g_1 \wedge g_2)$, $\bar{b} = \pm \frac{a}{3}[111]$.

It is thus concluded that the Burger's vector which satisfies the observed contrast conditions of visibility and invisibility is the $\frac{a}{3}$ <111> vector perpendicular to the loop plane, which is that expected for a Frank sessile loop. Inspection of the loops in fig. 3/4 shows that the surrounding Frank partial remains visible even when $\bar{g}.\bar{b} = 0$. In loop A for example which lies parallel to the foil surface only two opposite <110> edges are invisible in each <220> reflection and this side is parallel to

Table 1

Stacking Fault Contrast Behaviour

	Loop Plane	$\bar{R}$	g $\bar{2}20$ $\alpha = 2\pi g.R$	g $\bar{1}1\bar{1}$ $\alpha = 2\pi g.R$
A	111	$\frac{a}{3}$ 111	0	$-\frac{2\pi}{3}$
B	$\bar{1}\bar{1}1$	$\frac{a}{3}$ $\bar{1}\bar{1}1$	0	$-\frac{2\pi}{3}$
C	$1\bar{1}\bar{1}$	$\frac{a}{3}$ $1\bar{1}\bar{1}$	$-\frac{8\pi}{3}$	$+\frac{2\pi}{3}$
D	$\bar{1}11$	$\frac{a}{3}$ $\bar{1}11$	$+\frac{8\pi}{3}$	2π

(a)

Burgers Vector Analysis of Frank Loops

	Loop Plane and Possible $\bar{b}$	$g.b$ g [202]	$g.b$ g [$\bar{2}20$]	$g.b$ g [0$\bar{2}2$]	$g.b$ g $1\bar{1}\bar{1}$
A	$\pm\frac{1}{3}$ 111	0	0	0	$\pm\frac{1}{3}$
B	$\pm\frac{1}{3}$ $\bar{1}\bar{1}1$	$\pm\frac{4}{3}$	0	$\pm\frac{4}{3}$	$\pm\frac{1}{3}$
C	$\pm\frac{1}{3}$ $1\bar{1}\bar{1}$	$\pm\frac{4}{3}$	$\pm\frac{4}{3}$	0	$\pm\frac{1}{3}$
D	$\pm\frac{1}{3}$ $\bar{1}1\bar{1}$	0	$\pm\frac{4}{3}$	$\pm\frac{4}{3}$	1

(b)

the diffraction vector. This characteristic can be explained in terms of the properties of a general dislocation Hirsch (1965). For an edge dislocation there are two displacement components, one parallel to $\bar{b}$, $\bar{R}_1$ and the other normal to the slip plane $\bar{R}_2$. At the point r,ϕ in the plane normal to the dislocation

$$R_1 = \frac{b}{2\pi}\left[\phi + \frac{\sin 2\phi}{4(1-\nu)}\right]$$

and

$$R_2 = -\frac{b}{2\pi}\left[\frac{1-2\nu}{2(1-\nu)}\log|r| + \frac{\cos 2\phi}{4(1-\nu)}\right]$$

Combining these expressions with the displacement function of a screw dislocation, the displacement $\bar{R}$ for a general dislocation is

$$R = \frac{1}{2\pi}\left[b\phi + b_e\frac{\sin 2\phi}{4(1-\nu)} + b \wedge u \frac{1-2\nu}{2(1-\nu)}\ln|r| + \frac{\cos 2\phi}{4(1-\nu)}\right]$$

where $\bar{b}_e$ is the edge component of the dislocation, $\bar{u}$ is a unit vector along the positive direction of the dislocation line and ϕ is the angular co-ordinate in the plane normal to the line measured from the slip plane.

It can be seen that the general dislocation need no longer be visible if $\bar{g}.\bar{b} = 0$. Since an edge dislocation shows contrast when $\bar{g}.\bar{b} = 0$, to ensure complete invisibility the g.b $\wedge$ u component must also be zero. However, for a pure edge dislocation ($\bar{g}.\bar{b} \wedge \bar{u}$) varies around the loop and is only zero for those directions parallel to $\bar{g}$. This characteristic of the general dislocation has been used to good advantage in order to image the dissociation of the Frank partial into Shockley and stair-rod dislocations.

Intensity profiles calculated on the dynamical theory for the pure edge dislocation indicates that the image will be effectively invisible if the parameter $m = \frac{1}{8}(g.b \wedge u) < .08$. For Frank dislocations however $m \simeq .2$, and will thus cause strong contrast effects in certain <220> reflections even though $\bar{g}.\bar{b} = 0$. The contrast behaviour exhibited by the loops is

fully consistent with a dislocation being a Frank partial since m = 0 for those edges parallel to $\bar{g}$ and it is those edges which show no residual contrast effects in the three different <220> reflections.

3.5 Nature of the Frank Loops

The 'sense' of Frank loops has been analysed for both pure copper and Cu 16% Al, using two different methods. The traditional method in which $(\bar{g}.\bar{b})s \gtrless 0$ has been used for pure copper and the method proposed by Tunstall (1969) in which $g.b = \pm \frac{2}{3}$ has been used for Frank loops in Cu 16% Al. In this thesis $(g.b)\ s > 0$ has been defined to give outside contrast for interstitial loops when $\bar{b}.\bar{z} > 0$. Fig. 3/5(a) and (b) illustrates the method for electron irradiated copper, in which the diffraction vector $g = \pm[\bar{1}13]$ at beam direction $\bar{z} = [110]$. In this particular orientation, two loops 1 and 2 on the (111) and $(\bar{1}\bar{1}1)$ planes are at 35° inclination. The Frank partial is visible for both loops (g.b = 1) but the stacking fault is out of contrast since $\alpha = 2\pi$. The large loop (1) has been identified as $\bar{b} = \pm \frac{a}{3}[111]$, while the two smaller loops (2) have $\bar{b} = \pm \frac{a}{3}[\bar{1}\bar{1}1]$. Table 2(a) shows the expected contrast in both diffraction vectors. When $g = [\bar{1}13]$, the large loop exhibits outside contrast, while the small loops on the $(\bar{1}\bar{1}1)$ plane exhibits inside contrast. Reversal of g reverses the contrast. Considering the diffraction vectors giving outside contrast, loop 1 has been assigned $\bar{b} = \frac{a}{3}[111]$ and loop 2 $\bar{b} = \frac{a}{3}[11\bar{1}]$. Since $\bar{z} = [110]$ and $\bar{z}.\bar{b} > 0$ the loops are interstitial as expected.

The nature of Frank loops in copper aluminium alloys produced by electron irradiation have not been analysed before and for completeness, the results have been included. An exact check on the nature of these loops was also required in order to have complete confidence in the sense of dissociation of the Frank partial, which is discussed in this chapter.

Tunstall (1969) suggested a simpler analysis of Frank loops than could be made using the $(g.b)s \gtrless 0$ method. This analysis is based on the fact that under two beam conditions (reflection $\bar{g}$ excited) and at large

deviations from the Bragg condition w > 1, a dislocation with $\bar{g}.\bar{b}$ = $-\frac{2}{3}$ has a much weaker image than one with $\bar{g}.\bar{b} = +\frac{2}{3}$. The experimental procedure entails imaging the faults under conditions $\bar{g}.\bar{b} = \frac{2}{3}$ (w > 1). This can be satisfied when g = <200> at either $\bar{z}$ = <110> or <001>. The specimen was then tilted in a known direction along the Kikuchi band until the projected image width of the fault changed sufficiently to enable the plane to be indexed. The analysis of faults in Cu 16% Al is demonstrated in fig. 3/6. The foil normals are close to [101] and [110] and the loops are imaged in ± g [0$\bar{2}$0], micrographs (a), (c) and ± g [002], micrographs (c) and (d) under conditions which make $\bar{g}.\bar{b} = \frac{2}{3}$ for all the Frank partials.

Loop δ was recognized as being on the (111) plane since no stacking fault fringes were observed, due to the foil normal being cut along [111]. When $\bar{z}$ = [101], loop α was in broad projection and was indexed as being on the (1$\bar{1}$1) plane. The other two loops are in the near edge on position. (In fact the foil has been tilted about 10° from the [101] direction, to avoid other reflections contributing to the image) and thus some fringes can be seen on the γ and β planes. At the [110] foil normal however, loop α is at a shallow angle and was indexed as being on the (11$\bar{1}$) plane. The results of the analysis are shown in Table 2(b). Since the loop δ exhibits strong contrast when $\bar{g}$ = [002], g.b.= $+\frac{2}{3}$. The loop plane has been identified as (111) and the only Frank Burger's vector consistent with the results is a vector $\bar{b} = \frac{a}{3}$ (111). Since $\bar{z}$ = [120], $\bar{z}.\bar{b} > 0$; the loop is interstitial and the fault is extrinsic. Consider loop α; when $\bar{g}$ = [0$\bar{2}$0] strong contrast of the Frank results. For this contrast $\bar{g}.\bar{b} = +\frac{2}{3}$ and $\bar{b}$ must be $\frac{a}{3}$ (1$\bar{1}$1). Since $\bar{z}.\bar{b} > 0$, the loop is interstitial. In fact, all the Frank loops analysed were of extrinsic nature.

3.6 Multi-Layer Frank Loops

A very low incidence of double-faulted loops was observed during the irradiations and these were seen as irregular loops inside the parent Frank loop only in pure copper. Multilayer loops have

Table 2

Loop Sense Cu Using (g.b) s > 0 with g.b = 1

	Loop Plane	Loop $\bar{b}$	Outside Contrast	$\bar{b}$	$\bar{z}.\bar{b}$	Sense
Loop 1	111	$\pm \frac{1}{3}$ 111	g [$\bar{1}$13]	$\frac{1}{3}$ 111	> 0	int.
Loop 2	$\bar{1}\bar{1}$1	$\pm \frac{1}{3}$ $\bar{1}\bar{1}\bar{1}$	g [1$\bar{1}\bar{3}$]	$\frac{1}{3}$ 11$\bar{1}$	> 0	int.

(a)

Loop Sense Cu 16% Al using g.b $\pm \frac{2}{3}$

Loop Plane	Possible $\bar{b}$	Strong Contrast	$\bar{b}$	$\bar{z}$	$\bar{z}.\bar{b}$	Sense
δ	$\pm \frac{1}{3}$ 111	g [002]	$\frac{1}{3}$ 111	120	> 0	int.
γ	$\pm \frac{1}{3}$ 11$\bar{1}$	g [00$\bar{2}$]	$\frac{1}{3}$ 11$\bar{1}$	120	> 0	int.
α	$\pm \frac{1}{3}$ 1$\bar{1}$1	g [0$\bar{2}$0]	$\frac{1}{3}$ 1$\bar{1}$1	101	> 0	int.
β	$\pm \frac{1}{3}$ $\bar{1}$11	g [002]	$\frac{1}{3}$ $\bar{1}$11	101	> 0	int.

(b)

been reported by Westmacott (1961), Yoshida (1963) and Shimomura (1965) in quenched aluminium and also Edington (1965) who concluded that a slow quenching rate favoured the formation of double faulted loops in aluminium. Kritzinger (1969) observed multi-loops in quenched MgAl and evidence of heterogeneous nucleation of successive faults was obtained by Edington (1967) in studies of these three and four layer faults.

Interstitial double faults have been produced in proton irradiated Nickel and copper Mazey (1972) and in electron irradiated nickel by Urban (1970) and (1971). The analysis carried out by Mazey (1972) revealed that both his single faulted and inner loops were extrinsic and it is probable that they resulted from the clustering of a second plane of displaced interstitial atoms directly on top of the primary extrinsic fault or within several atom planes of the primary loop. A schematic model of a suggested sequence for a double interstitial on a (111) plane is shown in fig. 3/7. In this model, the outer loop of dislocation bounds an area of extrinsically faulted material in which normal ABCABC stacking sequence is shifted to BCA/C/BCA by the insertion of an atom layer. For the inner loop, the superposition of two interstitial planes does not involve any high energy violations of stacking, as is possible with quenched in double loops and the stacking sequence is ABCA/CABC, corresponding to an extrinsic stacking fault through the centre of the loop. The H.V.E.M. observations suggest that multi-layer loops only form in copper under high electron flux conditions (giving a high supersaturation of point defects), whereas only single-layer loops were observed at lower flux irradiations. Interstitials created near the compression side of the dislocation loop will tend to be repelled elastically towards the centre of the loop. The binding energy between the interstitial and the stacking fault will then hold the interstitials long enough to create the necessary supersaturation for the nucleation

of a new loop. The situation is more complicated in a thin foil where the distance to the foil surfaces is of the same order of magnitude as the loop diameter and there will be a depleted zone near the foil surface. Double and triple faulted loops have only been reported in pure metals and relatively dilute alloys, Al 3% Mg, all of which have a high stacking fault energy. It thus seems likely that the stacking fault energy of the metal influences whether double loops can form or not.

3.7 Frank Loop Shape

Previous studies of Frank loops in proton irradiated copper, Mazey (1968), and quenched copper aluminium alloys, Clarebrough (1966), have established that in general these loops adopt straight edges along <110> directions in the {111} planes. Calculations by Brown (1967) on the basis of anisotropic elasticity suggests that the equilibrium shape of Frank dislocation loops in copper may be hexagonal, but with <112> directions in the {111} planes. This configuration has been adopted by Frank loops when they are annealed, but has previously not been observed in loops under growth. According to Brown, the energy of the dislocations forming the loop depends critically on their line direction and at $\theta = 30^{\circ}$ corresponding to a dislocation along a $[1\bar{2}1]$ direction, the line energy is smallest.

Though the experimental and theoretical curves agree for pure aluminium, this agreement is not good in pure copper. It must be presumed that dislocation dissociation is playing a vital role in stabilizing the loop in the <110> orientations. The energy calculations of Gaboriaud and Grihle (1972) show that when dissociation is included, the energy of Frank loops is lower than that of circular loops. The Frank loops formed in copper and copper aluminium alloys do not restrict themselves to <110> loop edges, as fig. 3/8 illustrates. The loops develop <110> edges when they are small, but as they grow larger, irregular segments develop with edges along <112>, <321>, <532> and <891> in addition to

the original <110> edges. Sometimes loop-loop interactions cause the irregularity as fig. 3/11(b) loop A, though isolated loops at the foil centre also tend to exhibit the same behaviour, possibly as a result of pinning by impurities or more likely because the loop can climb more easily when it is undissociated. Weak beam micrographs of an irregular Frank loop with sides along <112>, <123> and <532> directions show that no dissociation is possible for this orientation.

Fig. 3/11(a) loop D shows a rectangular shaped loop with sides along $[0\bar{1}1]$ and $[\bar{2}11]$. Loops of all shapes have been observed, from triangles to the fourteen sided defect in fig. 3/11(b), loop C. However the directions of the loop sides are restricted to those mentioned above, presumably because the core energy is lowest in these particular orientations. Fig. 3/9(a) shows a large Frank loop in Cu 5% Al which has additional sides in the <211> directions. Loop (b) fig. 3/9 has developed its additional ledges after growing initially as a triangular loop. Quite clearly the superjogs on this loop have not been influenced by the presence of nearby dislocations or loops, though the loop is not quite so irregular as that of (a) where small dislocation segments at some stage in the loop growth have greatly influenced the shape.

If one compares the shape of Frank loops in pure copper figs 3/10 with those in Cu 16% Al, it is possible to observe differences between the two. Loops in Cu 16% Al generally form as triangles or regular hexagons and then gradually develop into large, very irregular loops, while loops in pure copper begin as hexagons and then transform into petal shaped loops. This shape is caused by the directional flow of interstitial atoms along the dilatational strain field gradient and is examined in more detail in Chapter 10. The fact that petal shaped loops were not observed in alloys >2 at% Al is rather puzzling. A possible explanation may be in the fact that the Frank dissociation width is about 25Å in pure copper and 140 - 170 Å in Cu 16% Al, making it very much

easier for constrictions to take place in copper. The petal loop shape implies that the jog density is much higher than that of a similar loop in Cu 16% Al and suggests that a different growth mechanism may exist.

Once constriction has taken place, the loop sides in copper will try and climb to <211> , which is reached in a short time. In the alloys there appears to be some resistance in rapid rotation to <211> and the sides remain along <213>. Brown's calculations for pure copper (1967) indicate that there is no dislocation energy minimum between <110> and <211>. However for Cu 16% Al which is more anisotropic, there may be subsidiary minimum, which could account for the other orientations observed.

Other reasons for the difference in shape may be:-

(1) The smaller observed sizes of Frank loops in copper. The greater degree of dissociation of the Frank loop in Cu 16% Al obviously stabilizes it against spontaneous nucleation of the Shockley partial dislocations. The loops in copper reach very much smaller sizes than in Cu/Al alloys, before surface or contamination stresses stimulate the removal of the stacking fault. Thus the petal shaped loops observed may only be a transition stage to the more irregular shaped loops as formed in the other alloys.

(2) It is possible that the directional flow of interstitials under the strain field of the loop may be modified by the large dissociation of the Frank partial onto the adjacent {111} plane.

(3) Differences in the loop growth process, since the curved shaped of loops in copper indicates a much higher jog density than for loops in the alloys.

The loop side directions of most (111) Frank loops in copper were impossible to measure due to this curvature.

(4) Changes in gas content of the copper foils. Several copper foils nucleated only triangular Frank loops, while other specimens polished at

different temperatures nucleated only hexagonal loops. The presence of an oxide layer on the foil surface also produced different types of Frank loops. In some copper foils for example, very few loops could be nucleated at any irradiation temperature until an oxide layer was established on the foil surfaces.

(5) Depth of the defect in the foil. Two triangular Frank loop orientations can be distinguished on the (111) plane parallel to the foil surface, each having a common side, but with the apex pointing in opposite directions. Triangular loops of one configuration nucleated at the top surface, while those of the other configuration nucleated near the bottom surface. In the centre some triangular defects were observed but the majority of loops had developed additional sides, thus forming irregular hexagons. Dissociation and the presence of vacancies in the foil must be affecting the loop shape in this manner.

In conclusion, the most common loop side direction in copper was found to be <110> and <112> while in Cu/Al alloys solute pinning or the low S.F.E. caused <123> and <532> sides to be observed.

3.8 Weak Beam Images of Dissociated Frank Loops

Since Hirsch and Silcox (1958) first observed stacking fault tetrahedra and postulated a mechanism of growth involving the dissociation of the Frank partial into a low energy stair-rod and a Shockley partial glissile on the inclined {111} planes, numerous observations of vacancy loops and tetrahedra have been recorded, but only recently have interstitial loops been readily observed as a result of H.V.E.M. irradiation. The partial dislocations involved had not been observed experimentally, but computer simulation of 'bright field' micrographs Clarebrough, Morton (1969) have suggested that such a reaction is possible.

Frank loops formed in the H.V.E.M. have been verified to be of extrinsic nature and to grow with edges along <110> directions. Using the Thompson notation, the Frank dissociation reactions possible are

Table 3

$\delta D = \delta\gamma + \gamma D$		
$\delta D = \delta\alpha + \alpha D$		Frank on δ plane
$\delta D = \delta\beta + \beta D$		
$\alpha A = \alpha\gamma + \gamma A$		
$\alpha A = \alpha\delta + \delta A$		Frank on α plane
$\alpha A = \alpha\beta + \beta A$		
$\beta B = \beta\alpha + \alpha B$		
$\beta B = \beta\delta + \delta B$		Frank on β plane
$\beta B = \beta\gamma + \gamma B$		
$\gamma C = \gamma\alpha + \alpha C$		
$\gamma C = \gamma\beta + \beta C$		Frank on γ plane
$\gamma C = \gamma\delta + \delta C$		

The Greek/Greek partials are stair-rods

The Greek/Roman partials are Shockleys

Possible Frank dissociation reactions into stair-rod dislocations at the intersection of {111} planes and glissile Shockleys on the inclined {111} planes.

given by table 3. That these reactions are permissible is given by Frank's rule

$$b_1^2 > b_2^2 + b_3^2$$

Thus for

$$b_1 = \frac{1}{3}[111],\ b_2 = \frac{1}{6}[110] \text{ and } b_3 = \frac{1}{6}[112]$$

$$\frac{1}{3} > \frac{1}{18} + \frac{1}{6}$$

Fig. 3/11 shows schematically the position of the partials involved in the reaction

$$\delta D = \delta\gamma + \gamma D$$

An intrinsic stacking fault as discussed by Hirthe and Lothe (1968), is formed when a layer of atoms is removed from the normal sequence, leaving ABC/BCA, while the extrinsic fault is formed by the addition of a layer of atoms to the normal sequence, giving ABCBABC. Only intrinsic stacking fault tetrahedra have been identified in metals, which suggests either that $\gamma_E > \gamma_I$ or that some other mechanism prevents the formation of extrinsic faults. However, Loretto (1966) and Gallagher (1966) have observed extrinsic faults in obtuse dislocation bands and in parallel dislocation interactions, their results suggesting that $\gamma_I \lesssim \gamma_E$.

Fig. 3/12 shows the possible dissociations expected for intrinsic and extrinsic Frank loops. In both cases, the fault on the inclined plane can make an acute or an obtuse angle with the original fault plane. In case (A) an intrinsic fault on the (111) plane can dissociate onto the $(\bar{1}\bar{1}1)$ plane, with the stair-rod $\delta\gamma$ at the intersection of these planes. Since δD points downwards, the Shockley Burgers vector γD points away from the stair-rod for the acute angle and towards it for the obtuse angle dissociation. Thus an intrinsic fault is formed when the angle is acute and an extrinsic fault formed when the angle is

obtuse. For case (B), (an extrinsic fault on the (111) plane) $D\gamma$ points away from the stair-rod for the obtuse intrinsic case and towards it for the acute extrinsic case. Recently R. Gaboriaud (1976) has compared the energies of intrinsic and extrinsic dissociated triangular loops for different γ_I/γ_E ratios in Silicon, with the conclusion that on an energetic basis an extrinsic S.F.T. is easier to nucleate than obtuse angled triangular defects. The technique was also applied to Cu/Al alloys with γ = 10 ergs/cm^2 with the conclusion that the obtuse angled triangular configuration would occur if $\gamma_I < \gamma_E$.

Using the weak beam technique or computer simulation, it is possible to determine the nature of faulted defects, since for interstitial defects, the Shockley partial will always be imaged on the outside of the stair-rod when dissociation has taken place. Conversely, for the vacancy Frank loops, Shockley's will be imaged inside the original loop.

The extent of the dissociation is governed by the balance between the decrease in elastic energy associated with the separation of the pair of partial dislocations and the increase in energy due to the generation of the stacking fault on the intersecting {111} plane. Thus this separation of partials depends on the stacking fault energy of the crystal. In low S.F.E. metals such as copper aluminium, the width of dissociation can be considerable.

Clarebrough and Morton (1969) have demonstrated that details of the contrast are sensitive to the separation of the Shockley and stair-rod dislocations. The main features of contrast under dynamical conditions which distinguished dissociated dislocations from undissociated dislocations were:-

(1) For <111> diffraction vectors ($g.b = \pm \frac{1}{3}$) when $g.u \neq 0$, a dark band of contrast crossed the light fringes.

(2) For <220> diffraction vectors in which g.R was integral, images were single and tended to be continuous, with strong contrast on one side

only. The strong contrast did not invert from side to side in ± g.

(3) For <020> diffraction vectors ($g.b = \pm \frac{2}{3}$) and $g.u = 0$ a distinct light band occurred between the edge of the dislocation image and the stacking fault fringes and there was no clear reversal of contrast between ± g. For $g.u \neq 0$ reversal of contrast between + g and - g depended on the beam direction. These results, though of interest are time consuming, expensive to produce and give little information on mechanisms of loop growth or shrinkage. Since both partials can be imaged in 'weak beam' conditions, direct information can be obtained concerning the behaviour of such loops.

Fig. 3/13 shows schematically Frank loops on the four {111} planes. The foil normal $\bar{F}$ was cut to be parallel to the [111] direction and thus loop δ on the (111) plane will exhibit uniform contrast across the stacking fault, since it is parallel to the foil surface. The other three loops α, β and γ are identical in that they are all inclined to the surface at an angle of 70°. Results from any one of these loop planes will then be completely representative of the other planes.

Foils of copper and copper aluminium alloys were prepared using methods described in Chapter 2. The specimens were then irradiated at elevated temperatures (≃ 250°C) in the hot stage so that large faulted Frank loops grew. The foils were then slowly cooled to room temperature, removed from the hot stage and transferred to a 100 keV microscope for analysis. To prevent foil bending, each was handled with extreme care using only vacuum tweezers.

3.9 Image Conditions for $\frac{a}{3}$[111] Frank Loops

The maximum tilt using the goniometer stage of the JEM.100B was ≃35°, which limited the usable beam directions. Thus in order to maximise the projected separation between the stair-rod and Shockley partials, the foils were tilted to <110> beam directions. Fig. 3/13(b) shows a Frank loop δ dissociating at an obtuse angle onto the γ plane. The angle of

Table 4

$\bar{z}$ [110] $\quad \frac{1}{3}\,\bar{1}\bar{1}\bar{1} = \frac{1}{6}\,\bar{1}\bar{1}0 + \frac{1}{6}\,\bar{1}\bar{1}\bar{2}$

	002	$\bar{1}11$	$1\bar{1}1$	$2\bar{2}0$	$1\bar{1}3$	$1\bar{1}\bar{3}$
111 S.F.	$\frac{4\pi}{3}$	$\frac{2\pi}{3}$	$\frac{2\pi}{3}$	0	2π	-2π
$\bar{1}\bar{1}1$ S.F.	$\frac{4\pi}{3}$	$\frac{2\pi}{3}$	$\frac{2\pi}{3}$	0	2π	-2π
$\frac{1}{6}\,\bar{1}\bar{1}0$	0	0	0	0	0	0
$\frac{1}{6}\,\bar{1}\bar{1}\bar{2}$	$-\frac{2}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	0	-1	+1

(a)

		$0\bar{2}2$	$2\bar{2}0$	$\bar{2}02$
	111 S.F.	0	0	0
	$\bar{1}1\bar{1}$ S.F.	$-\frac{8\pi}{3}$	$-\frac{8\pi}{3}$	0
	$\bar{1}\bar{1}1$ S.F.	$\frac{8\pi}{3}$	0	$\frac{8\pi}{3}$
	$1\bar{1}\bar{1}$ S.F.	0	$\frac{8\pi}{3}$	$-\frac{8\pi}{3}$
Aδ	$\frac{1}{6}\,\bar{1}2\bar{1}$	-1	-1	0
Bδ	$\frac{1}{6}\,2\bar{1}\bar{1}$	0	+1	-1
Cδ	$\frac{1}{6}\,\bar{1}\bar{1}2$	1	0	1
δα	$\frac{1}{6}\,\bar{1}0\bar{1}$	$-\frac{1}{3}$	$-\frac{1}{3}$	0
δβ	$\frac{1}{6}\,0\bar{1}\bar{1}$	0	$\frac{1}{3}$	$-\frac{1}{3}$
δγ	$\frac{1}{6}\,\bar{1}\bar{1}0$	$\frac{1}{3}$	0	$\frac{1}{3}$

(b)

$\bar{z}$ = [111]

$A\alpha = A\delta + \delta\alpha$ Theoretical

$B\beta = B\delta + \delta\beta$ Contrast

$C\gamma = C\delta + \delta\gamma$

projection between γ and the horizontal in this case is 35^{o}. In order to achieve best visibility of the partials, it is necessary that both the stacking faults be out of contrast and both dislocations be in contrast. These restrictions reduce the usable diffraction conditions.

Table 4(a) shows the values of g.b and 2πg.R for a Frank loop on the δ plane which can dissociate onto the γ plane. The beam direction is [110] and all possible diffraction vectors are indicated. The calculations suggest that the only usable diffraction vectors are g $[1\bar{1}3]$ or g $[1\bar{1}\bar{3}]$, since the stacking faults are out of contrast and the Shockley partial is in good contrast. Unfortunately, the stair-rod dislocation is always predicted to be out of contrast at any [110] beam direction, despite the diffraction vector chosen. Even the m ($\frac{1}{8}$ g.b Λ U) contrast is below visibility. Thus for $\bar{U} = [1\bar{1}0]$, $\bar{b} = \frac{1}{6}[110]$ and g = $[1\bar{1}3]$ m = -.09. It has however been possible to image the stair-rod under weak beam conditions though this necessitated the use of a highly stable top entry cartridge in the microscope, since exposure times of several minutes were required, depending on the foil thickness. The minimum thickness of foil in which defects formed was about 1200 Å, as a result of the denuded zones of 600 Å which appeared at each surface, caused by the diffusion of point defects to the foil surfaces under irradiation. Electrochemical back thinning techniques were tested in an attempt to reduce the specimen thickness after the loops had been formed, but severe etching resulted and the experiment was abandoned.

Figs 3/14 and 3/15 show micrographs of a triangular Frank loop formed in Cu 10% Al imaged at three <110> directions using g <111> and <113> diffraction vectors. Fig. 3/15(e) with g $[\bar{1}\bar{1}1]$ and z = [011], shows stacking fault on the inclined β plane outside the stair-rod dislocation, though this is not in contrast. The fringes imaged inside the triangle arose because the foil normal was not cut exactly on [111]. Fig. 3/15(g) shows both partials when imaged in g $[\bar{3}1\bar{1}]$, because g.b = $\pm$1

for the Shockley partial. The dislocation reaction along the $[0\bar{1}1]$ side is:-

$$\delta D = \delta\beta + \beta D$$

where βD is the outer partial.

This micrograph shows that the separation of Shockley and stair-rod partials is not constant along the dislocation length.

In fig. 3/15(h) where g = $[\bar{1}\bar{1}1]$ and z = [101], the stacking fault on the α plane is imaged. The $[\bar{1}01]$ side has developed during growth, additional <112> and <123> sides, which cannot dissociate, so that the partials must be constricted at these points. This occurred at points W and X and results in the $(\bar{1}1\bar{1})$ stacking fault terminating abruptly.

When g = $[1\bar{3}1]$ as in fig. 3/14(b), both partials on the α plane are imaged. Though the micrograph is not in good contrast, it is possible to detect the dissociation, which is partly covered by a dissociated $\frac{a}{2}$ <110> dislocation. The reaction of the Frank partial along this side is:-

$$\delta D = \delta\alpha + \alpha D$$

The stacking fault on the γ plane with its many discontinuities is imaged using g $[\bar{1}1\bar{1}]$, $\bar{z}$ [110] in micrograph (f). The same side, when imaged in g $[1\bar{1}\bar{3}]$ fig. (a) did not clearly resolve the partials, since some stacking fault is present on the γ plane. One of the difficulties experienced when using <113> diffraction vectors in weak beam conditions at <110> beam directions was the problem of avoiding other reflections being satisfied at the same time. In order to make the deviation parameter S = 2×10^{-2} Å^{-1}, g/2.4g was satisfied which, because of its orientation, brought <111> reflections into prominence. This effect was counteracted somewhat, by tilting 5 to 10° from the <110> axis, though this reduced the width of observable separation between the partials.

In 'strong' weak beam conditions $\simeq$ g/1.8g, the partials could be imaged near the <110> pole without the <111> reflections being strongly

satisfied, though at these values of S it becomes difficult to image the stair-rod. In general, a compromise was adopted using diffraction conditions midway between the two extremes discussed above. In micrograph 3/14(a) the effect of the [111] spots being satisfied can be observed, in that the stacking fault on the γ plane was imaged. It was consequently difficult to know if the stair-rod was being imaged since stacking fault fringes and stair-rod dislocations look similar. The dissociation reaction (if it could be observed) along the $[\bar{1}01]$ side would be:-

$$\delta D = \delta\gamma + \gamma D$$

The partial outline of the γD, $\frac{a}{6}$ [112] dislocation can be observed. Bright field micrographs figs. 3/14(c) and (d) are included for comparison with the corresponding weak beam images. Similar micrographs have been taken of copper and other copper alloys and these are shown in fig. 3/16.

Experimental results of the stair-rod and Shockley separations are shown in fig. 3/17, for the metals irradiated. Even though there is some considerable variation in the separations for the same alloy, it is clear that there is tentative agreement with the computer simulation results of Clarebrough and Morton (1969) and the loop energy calculations of Gaboriaud and Grihle (1972). Clarebrough's results for Cu 9.4% Al suggest a separation of between 60 - 80 Å, which implies that $(\frac{\gamma}{Gb})$ for this alloy is $\simeq 1.45 \times 10^{-3}$, while the Cu 15.6% Al results indicate a separation of 140 - 160 Å and $(\frac{\gamma}{Gb}) \simeq .65 \times 10^{-3}$.

Holmes (1975) has calculated the separation of partials expected under weak beam conditions and these results are discussed in Chapter 3/11. It is clear from the experimental results that great care must be exercized in the interpretation of weak beam micrographs. The main difficulty in comparing experimental results with computer calculations to determine the partial separation lies in the assumption that the measured separation is equal to the equilibrium separation. Stress in a thin foil may influence the separation of the Shockley/stair-rod

dislocations in a pure metal and stress, lattice friction, segregation etc. may influence the separation in alloys.

The foil stresses could arise from surface contamination, differential heating, overclamping of the foil in the holder, or image forces. Dynamic loop growth experiments have revealed that loop-loop interactions occur frequently, with an effect up to several hundred angstroms. The general manifestation of this result is that loops competing for interstitials may grow at different rates and develop large immobile superjogs, possibly as a result of the loop strain fields. Two parallel Frank loops have been observed to interact at distances of $\simeq$400 Å, this result indicating that the presence of nearby dislocations could well affect the equilibrium separation of the glissile Shockley dislocation on the inclined plane.

In fig. 3/15(f), dislocation z, which is a perfect dislocation of $\bar{b} = \pm \frac{1}{2}[1\bar{1}0]$, dissociating on the γ plane in the following reaction

$$\overline{DC} = \frac{1}{2}[110] = D\gamma + \gamma C$$

is within 500 Å of point Y, fig. 3/15(g). It can be observed clearly, that the separation of the partials at this point is twice that of the separation elsewhere along the dislocation. The Frank partial along $[0\bar{1}1]$ in fig. 3/15(f) is dissociating in the 'edge on' β plane towards the dislocation z, which is running from top to bottom in the foil at an angle of 35°. The dissociation of the Frank partial is not observed since the β plane contains the viewing direction.

Fig. 3/18 shows an enlarged view of a Shockley stair-rod dissociation in a Cu 10% Al foil. The section of the dislocation which is not constricted has a constant separation, while the dislocations (α) bounded by two constrictions a small distance apart are more widely dissociated. Since the acute corner does not have a stair-rod dislocation bounding the Shockley partials on the inclined planes, it could be assumed that the non equilibrium separation is caused by the presence of the nearby

Frank loop.

The influence of the surface on the width of constriction is difficult to ascertain without stereomicrographs in combination with weak beam pictures. However, it is unlikely that image forces are affecting the separation because the nearest surface must be ≏600 Å from the loop, as a consequence of the denuded layers. Foil stresses as a result of local heating, contamination or clamping were difficult to estimate due to the variations from specimen to specimen. In all the weak beam experiments performed, bend free and as far as possible contamination free foils were used. The nitrogen cold trap was in use at all times to cut down on contamination in the microscope, though even with this device, it became increasingly difficult after about ½ hour to take good micrographs.

Houska and Averbach (1959) have proposed that an ordering effect takes place in copper aluminium alloys at temperatures of about 200°C, which is responsible for an apparent increase in stacking fault energy. The behaviour of jogged dissociated dislocations has been explained by the presence of a uniform solute impedance in the alloy which is overcome by thermal activation on heating at low temperatures. McLean (1963) proposed this explanation to account for the behaviour of extended modes on heating, the results of which are shown in fig. 3/19(a). Corrected S.F.E. of Cu/Al alloys have been made by Koppenaal and Fine (1962) and are shown in fig. 3/19(b). Though solute impedance may be having some effect on the separations, it cannot account for a broadening of the spacing, since the S.F.E. is increased on heating. Hasegawa et al. (1974) have measured the S.F.E. of Cu 11% Al and Cu 16% Al using mode measurements at temperatures 20°C to 700°C. These authors record an increase in S.F.E. over this range. The results are confirmed by Saka (private communication) whose weak beam measurements of dissociated dislocations at elevated temperatures revealed a reduction in separation

at temperatures above 200°C with a minimum at 600°C. It seems quite likely that the separations measured in Cu 16% Al were those for the temperature of irradiation. The Shockleys at room temperature have probably been prevented from reaching the full separation by solute impedance effects.

Experimental results on the loop nature and densities from crystals grown at different rates yield some startling differences. Crystals of copper aluminium alloys grown at very fast rates, produced a large number of Frank loops in addition to perfect loops after irradiation at elevated temperatures in the H.V.E.M. When the same alloys were grown at a speed seven times slower, only rhombus perfect loops nucleated and grew. Since all the weak beam results of Frank partial separations are from fast grown crystals, it seems likely that non-homogenization of the crystal may also have promoted the non-equilibrium separations. The wide spread of experimental results of Frank partial dissociations in the Cu 10% Al crystals has probably also been influenced by the fact that foils were cut from different parts of the crystal. Thus the separations measured in this series of experiments in the Cu 10% Al and Cu 16% Al specimens should be treated with caution.

Gaboriaud and Grilhe (1972) have computed the energies of hexagonal Frank loops taking into account the dissociation of the partial Frank dislocation surrounding the defect, and the energies compared to undissociated Frank loops, circular loops and other classical defects. The Shockley partial fig. 3/20(c) has been approximated by three segments AD, DC and CB, each having the same burgers vector as the original curved Shockley partial shown. The areas of the stacking faults under the partials have been adjusted to be equal. The total interaction energy using Kroner's continuum theory of dislocations requires the calculation of 270 energies between straight segments. The results are shown in fig. 3/20 for Cu 13% Al an alloy where $(\frac{\gamma}{Gb}) = .7 \times 10^{-3}$. Graph (A) compares the

energies of undissociated hexagons, circular loops and dissociated hexagons as a function of $^{h}/b$ for $\alpha = 45^{o}$, where α = angle between the Shockley and stair-rod dislocations as shown in fig. (C). It is clear from these results that in low stacking fault energy metals dissociation takes place. Fig. (B) shows that the energy of a hexagonal loop as a function of α has a minimum value of $\alpha = 37^{o}$, in agreement with the measurements of $40^{o} - 45^{o}$ made on Cu 10% Al alloys for the angle between the tangent to the Shockley partial and stair-rod dislocations. Undissociated hexagons are unlikely to occur in any metal and in specimens where the stacking fault energy is so high as to preclude dissociation, the optimum shape of the loop will be circular, as is the case for aluminium.

3.10 Dissociation of Frank Loops on the α, β and γ planes

Fig. 3/13(c) shows the orientation of loops α, β and γ at $z = [111]$. The loops are inclined at 70^{o} to the beam direction and can dissociate onto the δ plane (parallel to the foil surface) or onto two of the other {111} planes which are steeply inclined to the beam direction. Table 4(b) illustrates the theoretical contrast expected when each of the {220} diffraction vectors are used to image the partial dislocations.

Micrographs 3/21 - 3/24 illustrate the structure of inclined Frank loops when imaged in weak beam diffraction conditions at [111], <110> and <112> beam directions. Loops H_{β} and S are representations of loops of this type, whose structure can clearly be seen in fig. 3/24 where the diffraction conditions are $g = [\bar{2}20]$, $z \simeq [113]$. Loop H on the $(\bar{1}1\bar{1})$ plane exhibits fringe contrast from this stacking fault and also from the steeply inclined dissociation fault on the α plane. The Shockley partial $\bar{A}\delta$ on the (111) plane is clearly visible, while the enclosed stacking faults on this plane is out of contrast.

The dissociation width of loop H_{β} appears to depend on the separation of the constrictions. As the distance between constrictions reduced, so the partial separation appeared to become smaller. Assuming the

angle between the Shockley and stair-rod remains constant at $\simeq 40^{\circ}$, then the minimum distance between constrictions for the full partial separation of say 140 Å will be

$$\frac{2 \times 140 \text{ Å}}{\tan 40^{\circ}} = 340 \text{ Å}.$$

Any constriction separation below this would tend to give rise to a non-equilibrium separation of partials. The actual separation between the short constrictions is about 280 Å, while that of the longer segment is $\simeq 970$Å. On the extreme right of the Shockley partial $\bar{A}\delta$ of this loop there is a very short segment of about 200Å which has a dissociation width very much smaller than the 280Å length segment.

Fig. 3/24 also shows that loop (S) on the $(1\bar{1}\bar{1})$ plane has its stacking fault on the $\beta(1\bar{1}\bar{1})$ plane, visible as well as the partial $\bar{B}\delta$ dissociated onto the δ plane. The stair-rod dislocations are not visible as a result of the presence of the inclined stacking fault.

The inclined loops have also been imaged in fig. 3/23 at the <211> beam direction using g = <111>; the micrographs showing stacking faults on the inclined planes and uniform contrast from the stacking faults on the (111) δ plane.

3.11 Weak Beam Images of 300° Loop Corners

Weak beam micrographs and annealing experiments reported in this thesis have established that dissociated Shockley partial dislocations at 60° and 120° corners of Frank loops are constricted as shown in fig. 3/27. Fig. (A) precludes the formation of extrinsic stacking fault tetrahedra and also allows triangular or hexagonal loops to anneal at the same rate. Dissociated loops with these two angles are most commonly observed, but it is possible for Frank loops to grow with re-entrant corners, so that the dissociated Shockley partials are not constricted at the corner.

Fig. 3/25 shows schematically the reaction. For the (111) Frank

loop parallel to the foil surface, the dissociation reactions that will occur at the loop edges are:-

$$\frac{a}{3}[111] = \frac{a}{6}[112] + \frac{a}{6}[110] \text{ on the } \gamma \text{ plane}$$

and $$\frac{a}{3}[111] = \frac{a}{6}[121] + \frac{a}{6}[101] \text{ on the } \alpha \text{ plane.}$$

Fig. (A) demonstrates the position of the Shockleys looking from the [111] direction. Since the stacking faults enclosed by the Shockley and stair-rod on the inclined planes are intrinsic, both Shockleys glide in the same direction. The partials $\frac{a}{6}$ <121> bow out on the inclined faces and meet one another, forming new dislocations of the type $\frac{a}{6}$ <110>. In fig. (B) the following reaction takes place:-

$$\frac{a}{6}[112] - \frac{a}{6}[121] = \frac{a}{6}[0\bar{1}1]$$

The resultant dislocation being a low energy stair-rod at the intersection of the $(\bar{1}1\bar{1})$ and $(\bar{1}\bar{1}1)$ planes. Fig. (B) illustrates the nature of the reaction as seen from the [111] beam direction. Since it is not possible to image both stair-rod and Shockley at this normal, the specimen was tilted to z = [110] and imaged in g = $[1\bar{1}\bar{3}]$, as shown in fig. (C). Fig. 3/26 shows micrographs of a 300° corner of a Frank loop in Cu 10% Al taken in g <111> and <113> reflections. Fig. 3/26(c) clearly shows the stacking fault contrast on the inclined $(\bar{1}1\bar{1})$ plane, while fig. (A) demonstrates that the Shockley partial can be pulled out to almost twice its equilibrium separation (156Å). In this orientation, the stair-rods $\frac{a}{6}[0\bar{1}1]$, $\frac{a}{6}[101]$ and $\frac{a}{6}[121]$ are superimposed, but the effect of the presence of the additional $\frac{a}{6}[0\bar{1}1]$ stair-rod can be observed.

The other configuration that can be observed in the same micrograph is the 240° corner. Both Shockley partials must dissociate in the upward direction fig. 3/25(d), to maintain an intrinsic fault between the dissociation, which necessitates constriction at the corner. Therefore, only in the 300° corners can a low energy stair-rod link the dissociated gliding Shockley partial dislocations.

3.12 Weak Beam Images of Partially Annealed Frank Loops

Extrinsic Frank loops having <110> edges have been shown to dissociate into Shockley and stair-rod partials to lower the loop energy. Calculations by Gaboriaud and Grihle (1972) show that the energy of a dissociated hexagonal loop is considerably less than that of a circular loop having the same number of precipitated interstitials. Hence the loops grow with sides along <110> directions. When the loops are annealed however, vacancies left in the foil, being mobile, attach themselves to the loop corners. Jogs run from the corners, gradually forcing the loop sides to change from $[1\bar{1}0]$ say, to $[2\bar{3}1]$, $[3\bar{5}2]$ and $[1\bar{2}1]$ fig. 3/27(c).

When the loop is in the <112> edge form, jogs are in plentiful supply and since dislocations along <112> directions cannot dissociate, the shrinkage of loops is probably controlled by the motion of jogs along the undissociated Frank dislocation. That the loop cannot dissociate when its sides are along $[1\bar{2}1]$ can be seen from fig. 3/28, which shows a Frank loop in a Cu 7% Al specimen formed by irradiation at 220°C in the H.V.E.M., and then annealed in situ for 10 minutes at this temperature.

Loop α which lies on the (111) plane, was imaged under weak beam conditions g $[1\bar{1}3]$, z [110] and can dissociate onto the γ $(\bar{1}\bar{1}1)$ plane, with an angle of projection 35°. The reaction $\delta D = \delta\gamma + \gamma D$ can be observed clearly along the $[1\bar{1}0]$ direction at x, however along the $[1\bar{2}1]$ direction at z, no such splitting is visible; only the Frank partial being imaged.

Loop β, which lies on the γ plane, can dissociate onto the δ (111) plane along the $[1\bar{1}0]$ direction as shown. In this reflection, stacking fault fringes are not predicted to be visible in the loop with $b = \frac{a}{3}[\bar{1}\bar{1}1]$ and it has been presumed that while weak beam conditions were being established for the diffraction vector g $[1\bar{1}\bar{3}]$, interference from the <111> reflections, caused fringes to appear. However, this

does not in any way detract from the fact that dissociation was observed only along $[1\bar{1}0]$ directions.

Two other points of interest emerge from this micrograph:

(1) The stair-rod dislocation of the inclined loop gives much greater contrast than the same stair-rod of the (111) loop, parallel to the surface.

(2) At point Y, loop β is constricted along the $[2\bar{1}\bar{1}]$ direction. The distance between constrictions to the right of Y is about 200 Å and the non-equilibrium separation of partials about 40 Å. The larger segment to the left of Y is ≏450 Å in length and has the equilibrium spacing of ≏55 Å.

The annealed Frank loop with sides along $[1\bar{2}1]$ directions is metastable since calculations show that for Cu and Cu/Al alloys, a circular defect always has a higher energy than a dissociated Frank loop, and a lower energy than an undissociated hexagonal Frank loop, except when the stacking fault energy >150 ergs/cm^2. Brown (1967) predicted that the lowest energy form of an undissociated Frank loop in Cu has sides along <112>, instead of being exactly circular. For Cu 16% Al however other low index directions have been observed along <123> and <532>.

To account for this, it is assumed that in the transition from <110> to <112> directions there are energy minima at these positions. Brown's conclusion that large Frank loops tend to a circular shape is not borne out in the present experiments since large loops are found with <110> edges. In conclusion, the weak beam micrographs of annealed loops indicate that dissociation is not possible along directions other than <110>, though the micrographs are not of sufficient quality to postulate an annealing mechanism.

3.13 Image Computation of the Contrast Expected from the Dissociation Reaction $D\delta = D\gamma + \gamma\delta$

Holmes (1975) has calculated five beam images in $\pm [1\bar{1}3]$ reflections, using anisotropic elasticity together with the elastic constants for Cu 10% Al. The geometry used in the calculations is shown in fig. 3/29. d

represents the distance of the loop to the foil surface, while t' is the thickness of the foil in the [110] direction. The Shockley configuration (B) has been used since this partial is imaged on the outside of the stair-rod in weak beam micrographs of interstitial Frank loops. The upward foil normal has been defined as F [111], while the beam direction is z [110]. As the loops imaged in this investigation are large (.2μ), the dissociating side has been treated independently as two parallel infinite dislocations.

The requirements that {113} reflections be used have been discussed earlier in this chapter. At the <110> pole there are two sets of <113> vectors, but without loss of generality the computations have been restricted to g ± [1$\bar{1}$3], since both partials along the [1$\bar{1}$0] direction are pure edge and no component of the displacement $\bar{R}$ is in the line direction. Under these conditions, $|g.b| = 1$ for the Shockley partial, so that strong contrast will occur. However, $|g.b| = 0$ and $|g.b \wedge U| = .7$ for the stair-rod so that only weak contrast results. In the parallel beam computations, a deviation parameter of $S = 2.14 \times 10^{-2}$ Å^{-1} corresponding to g/2.4g was used.

Fig. 3/30 shows the position of the peaks, with the dissociation width $\Delta = 79$ Å and the stair-rod set at a depth d from the foil surface of 1.0 ξ_g ($\xi_g = 536$ Å). Considerable variation of peak position can be observed as a function of specimen thickness. Because both partials have large values of $(g.b \wedge U)$, they can give rise to two distinct peaks. Clearly no correction factor can be determined, to give the exact position of partials. Images of a Frank partial dissociated by 79 Å placed at two depths of $d = 1.00\ \xi_g$ and $d = 1.04\ \xi_g$ were computed for foils $t' = 2.00 - 2.2\ \xi_g$. Over this small range, the images varied enormously. Fig. 3/31(a) shows images computed using g [1$\bar{1}$3], of a defect at two depths in a foil of thickness $2.08\ \xi_g$. Quite clearly, the experimental images and computed images do not agree.

In order to eliminate the effects of depth and thickness, Holmes (1975) incorporated the effects of beam divergence into the image computations. Intensity oscillations have a periodicity with foil thickness and defect depth given by the effective extinction distance. If the illumination is considered to be divergent, there is a spread in S values given by $\Delta S = g\alpha$ and the image profile may be calculated using

$$|\phi_g(\alpha,z)|^2 = \iint |\phi_g(k,z)|^2 \, I(k)\,dK_x\,dK_y$$

where $\phi_g(k,z)$ is the amplitude in beam g, in a column at depth z assuming a parallel incident beam of wave vector k, and $I(k)\,dK_x\,dK_y$ is the probability that an incident electron has x and y components of the wave vector in the range k_x, $k_x + dk_x$ and k_y, $k_y + dk_y$. The angular divergence α_{max} determined by the C_2 aperture was found by measurement of diffraction spot size to be

$$\alpha_{max} \simeq 2.5 \times 10^{-3} \text{ rdn's.}$$

This averaging process should effectively reduce the magnitude of depth and thickness variations in the image. The spread in s values corresponds to a spread in effective extinction distances and Holmes has concluded that defects which lie at depth d

$$d \geq \frac{1}{2}\left(\frac{1}{\Delta s}\right)$$

$$\geq 250\text{Å}$$

have image oscillations reduced, though with slightly increased peak width.

Melander and Sandstrom (1974) have assessed the importance of the beam divergence theoretically while Holmes (1975) has compared micrographs of fully divergent beam images and almost parallel beam images. In the latter, intensity oscillations along the dislocation length are pronounced.

Foils which have been irradiated in the H.V.E.M. at elevated temperatures have zones $\simeq$500 Å thick at each surface, free of defects. The Frank

loops under investigation are parallel to the foil surface and so divergent beam calculations can be used with confidence. Fig. 3/31(b) shows the $[1\bar{1}3]$ divergent beam images for the defect geometry corresponding to fig. 3/31(a). The images resemble those observed experimentally and it is clear that oscillation effects have been reduced. The shaded regions in fig. 3/30 indicate the position in which the divergent beam images of stair-rod and Shockley lie. The stair-rod gives rise to two peaks symmetrical about the partial position, giving a very low intensity broad image. The Shockley partial now has only one peak of high intensity and for g $[1\bar{1}3]$ lies outside the partial position. When the diffraction vector was changed to g $[\bar{1}1\bar{3}]$ the peak lay between the partials and thus inside/outside contrast can be observed. The variation in the Shockley and stair-rod peak position as a function of foil thickness t', defect depth d and partial separation have also been calculated, using the divergent beam approach. The general conclusion is that though there is small oscillation of the peak position around the partial, the contrast is well behaved and relations between the observed separation and true separation can be predicted. These are:-

$$1\bar{1}3 \text{ outside } \Delta = \Delta_{obs} - 7.5 \pm 7.5 \text{ Å}$$

$$\bar{1}1\bar{3} \text{ inside } \Delta = \Delta_{obs} + 7.0 \pm 7.5 \text{ Å}$$

The results obtained for copper alloys are illustrated in fig. 3/17. Calculated separations of Shockley and stair-rod reactions are shown as a function of stacking fault energy for each material. The stacking fault energies are those derived by Ray (1971). The observed separations are plotted together with the real separation which depended on whether the loops were in inside or outside contrast. The experimental separations come within the calculated values for the low alloy concentrations. However, though several loops were analysed for each alloy, only two foils for each of these alloys were of sufficient quality to give measurable

images. The separations for the Cu 10% Al and Cu 16% Al alloys varied considerably probably due to the non-homogeneity of the crystals, since measurements were made on foils cut from the bulk crystal over a period of some months. The variation along the length of a dislocation can probably be explained in terms of solute impedance effects as discussed earlier in this chapter.

Calculations have only been carried out for loops on the (111) plane parallel to the foil surface for the reaction $D\delta = D\gamma + \gamma\delta$, with $D\gamma$ dissociated near the electron entrance surface. However, the other side of the loop can dissociate with the Shockley dissociated towards the electron exit surface. At the [110] zone axis, the Frank loops on $(\bar{1}\bar{1}1)$ planes can dissociate as shown in fig. 3/13(d). In this configuration, the loop grows towards the foil surface and the dissociation plane (111) is parallel to the foil surface. Quite clearly the geometry is different and it is conceivable that different image profiles may result.

Only rough estimates of dissociation can be obtained from loops on these planes. Two interesting differences have been observed between dissociation reactions,

$$D\delta = D\gamma + \gamma\delta$$

and

$$\gamma C = \gamma\delta + \delta C$$

The stair-rods $\bar{\gamma}\bar{\delta}$ of loops on the δ plane are difficult to image, while the same stair-rod formed by loops on the γ plane are easily visible. Secondly, the Shockley and stair-rod dislocations of (111) plane loops exhibit widely varying separations along the dissociated side, while γ plane loop separations are almost constant along the side. Since the loops on the γ $(\bar{1}\bar{1}1)$ planes are inclined at 70° to the foil normal, it is likely that the dissociation takes place close to the surface, possibly within 250 Å. In this case the divergent beam calculations cannot be applied. It is assumed that depth effects can help to image that stair-rods of such loops in strong contrast.

If impurities pin the Shockley partial into non-equilibrium positions, it is possible that surface image forces overcome the pinning, making the separation along the dissociating side constant. Variations have also been observed, in the visibility of the stair-rod $\bar{\gamma}\bar{\delta}$ from loops on the (111) plane as a function of deviation parameter S. When g/2.4g was satisfied ($S = 2.14 \times 10^{-2}$ Å^{-1}), the stair-rod appeared in good contrast. However after a tilt to $S = 1.53 \times 10^{-2}$ Å^{-1} the stair-rod was only in very weak contrast, if at all visible. The corresponding stair-rod imaged in a loop on the $(\bar{1}\bar{1}1)$ plane always exhibited good contrast. It appeared that as the deviation parameter increased, the visibility of the stair-rod increased, for the order of S used in this thesis. It is possible that the dislocation $\gamma\delta$ was being tilted into the Bragg reflection, as the value of S changed, thus improving the visibility.

3.14 The Unfaulting of Interstitial Frank Loops

Observations of the unfaulting of Frank sessile dislocation loops in F.C.C. metals to produce perfect dislocation loops have been reported by Cotterill (1963), Whelan (1963) and the energetics of the unfaulting process has been discussed by Cotterill (1963)(1965), Kuhlmann-Wilsdorf (1965). Perfect loop rotation and self climb of loops in Al .13 Mg has been analysed by Swart (1973), in which the hexagonal prismatic loops produced by the unfaulting of Frank vacancy loops, are shown to undergo rotation about an axis parallel to their pure edge sides from the original {111} orientation to an orientation close to {110}.

The simultaneous action of two shearing Shockley dislocations to remove the Frank stacking fault of vacancy loops has been discussed by Swart and Kritzinger (1974), while the unfaulting of interstitial Frank loops has been observed by Spring (1970) and Mazey (1972). The exact mechanism for the unfaulting reaction is not clear and it is unusual in most metals to be able to record the unfaulting reaction because of the speed with which the partials cross. However, in Cu 16% Al, the unfaulting

process takes place so slowly that it is possible to record the dislocations as the fault is being cleared.

The unfaulting process involves in the case of intrinsic loops, the nucleation of a single shearing Shockley dislocation within the stacking fault of the Frank loop and its propagation over the faulted area. In the case of extrinsic Frank loops, however two Shockley partial dislocations are required to clear the fault, one above and one below. The possible dislocation reactions are shown in table 5(A). The resulting hexagonal perfect dislocation loop initially has the same (111) orientation as the original Frank loop, but it may subsequently rotate to a near edge orientation. The energy required to nucleate the partial dislocations arises as a result of stresses in the thin foil from contamination, heating, loop-loop interaction or instability at large loop sizes.

The shearing reaction was observed in alloys of Cu .077% Al and Cu 16% Al, but great difficulty was experienced in relating isolated perfect loops with the original Frank loops. Normally, the sheared loops interacted with the foil surface, or linked up with other loops or dislocations, making analysis of final orientation very difficult. However, on the occasions when the perfect loops remained free from other dislocations, the loop plane was analysed using the projected directions of the loop sides.

Fig. 3/32(b) shows two large perfect loops α and β in a foil of Cu .077% Al with Burger's vector $b = \frac{a}{2}[1\bar{1}0]$, which sheared from Frank loops on the $(\bar{1}1\bar{1})$ planes. The sides of loop α have been analysed to lie along $[54\bar{1}]$, $[31\bar{2}]$, $[011]$ and $[110]$ indicating that the perfect loop plane is $(\bar{1}1\bar{1})$. The plane of loop β could not be analysed exactly as a result of the curvature of the loop sides. The loop plane appears to lie in two orientations, indicating that partial rotation towards $n = (0\bar{1}1)$ has taken place. After further irradiation, the perfect loops in dilute alloys rotated about 8 or 9 degrees, from the {111} plane. None of the

Table 5

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

$$\frac{111}{3} + \frac{\bar{1}2\bar{1}}{6} + \frac{2\bar{1}\bar{1}}{6} = \frac{1}{2}[110] \qquad \delta \text{ plane.}$$

$$\frac{111}{3} + \frac{\bar{1}\bar{1}2}{6} + \frac{2\bar{1}\bar{1}}{6} = \frac{1}{2}[101]$$

$$\frac{\bar{1}1\bar{1}}{3} + \frac{\bar{2}\bar{1}1}{6} + \frac{1\bar{1}\bar{2}}{6} = \frac{1}{2}[\bar{1}0\bar{1}]$$

$$\frac{\bar{1}1\bar{1}}{3} + \frac{121}{6} + \frac{1\bar{1}\bar{2}}{6} = \frac{1}{2}[01\bar{1}] \qquad \alpha \text{ plane.}$$

$$\frac{\bar{1}1\bar{1}}{3} + \frac{121}{6} + \frac{\bar{2}\bar{1}1}{6} = \frac{1}{2}[\bar{1}10] \qquad \text{(A)}$$

$$\frac{1\bar{1}\bar{1}}{3} + \frac{211}{6} + \frac{\bar{1}\bar{2}1}{6} = \frac{1}{2}[1\bar{1}0]$$

$$\frac{1\bar{1}\bar{1}}{3} + \frac{\bar{1}1\bar{2}}{6} + \frac{\bar{1}\bar{2}1}{6} = \frac{1}{2}[0\bar{1}\bar{1}] \qquad \beta \text{ plane.}$$

$$\frac{1\bar{1}\bar{1}}{3} + \frac{\bar{1}1\bar{2}}{6} + \frac{211}{6} = \frac{1}{2}[10\bar{1}]$$

$$\frac{\bar{1}\bar{1}1}{3} + \frac{112}{6} + \frac{1\bar{2}\bar{1}}{6} = \frac{1}{2}[0\bar{1}1]$$

$$\frac{\bar{1}\bar{1}1}{3} + \frac{112}{6} + \frac{\bar{2}1\bar{1}}{6} = \frac{1}{2}[\bar{1}01] \qquad \gamma \text{ plane.}$$

$$\frac{\bar{1}\bar{1}1}{3} + \frac{\bar{2}1\bar{1}}{6} + \frac{1\bar{2}\bar{1}}{6} = \frac{1}{2}[\bar{1}\bar{1}0]$$

Possible Frank sessile → perfect loop dislocation reactions involved on each of α, β, γ and δ planes due to the passage of shearing Shockley partial dislocations.

g	$\bar{1}1\bar{3}$	$1\bar{3}\bar{1}$	$\bar{3}\bar{1}1$	$\bar{2}02$
$C\delta$ $\frac{1}{6}[\bar{1}\bar{1}2]$	-1	0	1	$^2/_3$
$B\delta$ $\frac{1}{6}$ $2\bar{1}\bar{1}$	0	1	-1	-1
$A\delta$ $\frac{1}{6}$ $\bar{1}2\bar{1}$	1	-1	0	0

(B)

perfect loops analysed were found to lie on {110} planes, the majority lying between {111} and {110} planes, depending on the alloy concentration. The sheared loops in the dilute alloys were found to rotate much more than corresponding loops in Cu 16% Al specimens, all of which remained on the {111} planes. The other loops in fig. 3/32 have sheared as follows:-

Frank Plane $(\bar{1}1\bar{1})$	Frank Plane $(1\bar{1}\bar{1})$	Frank Plane $(\bar{1}\bar{1}1)$
Loop 1 b = $\frac{1}{2}[1\bar{1}0]$	Loop 6 b = $\frac{1}{2}[1\bar{1}0]$	Loop 7 b = $\frac{1}{2}[10\bar{1}]$
Loop 2 b = $\frac{1}{2}[0\bar{1}1]$		Loop 8 b = $\frac{1}{2}[0\bar{1}1]$
Loop 3 b = $\frac{1}{2}[0\bar{1}1]$		Loop 9 b = $\frac{1}{2}[10\bar{1}]$
Loop 4 b = $\frac{1}{2}[1\bar{1}0]$		
Loop 5 b = $\frac{1}{2}[0\bar{1}1]$		
Loop 10 b = $\frac{1}{2}[1\bar{1}0]$		

It can be seen that for the $(\bar{1}1\bar{1})$ and $(\bar{1}\bar{1}1)$ planes, two of the three resultant Burger's vectors are visible. Examples of loop interactions can also be observed in the micrographs at points x, y and z (see fig. 3/32(c)). x shows the interaction of loop 3, b = $\frac{1}{2}[0\bar{1}1]$ with loop 4, b = $\frac{1}{2}[1\bar{1}0]$. These loops have joined together with the side of b = $\frac{1}{2}[10\bar{1}]$ common to both loops. This form of reaction is very common, when perfect loops are developing into dislocation tangles. The reaction at y is more interesting, in that two Frank loops of b = $\frac{a}{3}[\bar{1}1\bar{1}]$ have interacted with the subsequent complete removal of the common side parallel to the [011] direction. The fact that the stacking fault remained intact is puzzling, since normally loop interactions result in stacking fault shear. At point z, two loops having b = $\frac{a}{2}[0\bar{1}1]$ have intersected, without the annihilation of the intersecting side. It is presumed that the two partials are very close together, but with opposite Burger's vectors.

Fig. 3/33 shows another set of perfect loops in Cu .077%Al, though

only two, α and β, can be positively identified and related to Frank loops. Loop α has been identified as having $b = \frac{a}{2}[10\bar{1}]$, with its original loop plane as $(\bar{1}\bar{1}1)$. In fig. (D), the long diameter has a projection of 7° off the $[\bar{1}10]$ direction towards $[\bar{1}2\bar{1}]$. Pure edge loops can be identified very easily, since the projection lies along the [112] orientation. Loop β is more interesting in that it clearly shows two orientations, one along $[1\bar{2}1]$, and the other 8° from $[\bar{1}10]$. Part of this loop has been able to rotate to the pure edge orientation, while the other part is still in the process of rotation.

Fig. 3/34 illustrates the transformation of Frank loops in a Cu 16% Al specimen. Of particular interest, are loops 1, 2, 3 and 4, which have nucleated and grown as triangular or hexagonal loops, then sheared by the passage of Shockley partials into loops with $b = \frac{1}{2}[101]$, but still lying on the original (111) loop plane. Loops 5, 6, 7, 8 and 9 on the $(\bar{1}1\bar{1})$ plane, all sheared to $b = \frac{a}{2}[011]$. Loop 10, with its initial Burger's vector of $b = \frac{a}{3}[\bar{1}1\bar{1}]$ sheared spontaneously to $b = \frac{a}{2}[0\bar{1}1]$, but still retained its loop normal as $n = [\bar{1}1\bar{1}]$ and sides along $[\bar{1}01]$, [011] and [110]; the sides along [011] being of edge character. Perfect prismatic loops are not often found lying on {111}planes, either because they nucleate directly on {110} or because they can lower their energy by rotation from {111} to ≙ {110} places, so as to be perpendicular to their Burger's vector. This latter mechanism has been proposed to account for the observations of rhombus loops on {110} planes. However, such rotation was not observed during the experiments carried out for this thesis.

In a hexagonal perfect loop, only four out of the six segments are glissile (those along $[\bar{1}01]$ and [110] for loop 10) the other two segments being pure edge (along [011]). In such cases rotation of the loop plane can only occur if atoms can be redistributed around the loop perimeter. This may be due to self climb by pipe diffusion, in which interstitials

formed on one side of the loop, find an easy migration path along the dislocation line. During growth, the climb of dislocations apparently takes place more rapidly at undissociated dislocations. In Cu/Al alloys the perfect hexagonal loops have not been observed to rotate to rhombic form, suggesting that the pure edge sides are not being eliminated. In these materials the edge sides appear to be the most stable. Even the movement of non-edge sides is restricted, though loop 11 shows some evidence of trying to change to a pure edge configuration.

Thus while Swart (1971) was able to observe loop rotation in Al/Mg alloys after shear, it has not been possible in the present series of experiments to repeat the observation. Some partial rotation of perfect loops in Cu .077% Al was observed, but loop rotation in Cu 16% Al was not observed. Since the S.F.E. of Al 1% Mg is very high, the Shockley separation will be correspondingly very low, allowing rapid rotation to a near edge configuration. It seems likely that the degree of separation of Shockley partials plays a large part in determining the final orientation.

3.15 Weak Beam Images of the Unfaulting Reaction

Fig. 3/35 is a schematic diagram of a Frank loop on the (111) plane, which has its stacking fault partially removed, whilst figs 3/36 and 37 show the contrast observed in different diffraction vectors. The theoretical visibility for Shockley partials on the (111) plane is illustrated in table 5(B).

When g = $[\bar{1}1\bar{3}]$, dislocation 1 is out of contrast, while in g $[1\bar{3}\bar{1}]$ all dislocations are in contrast. g = $[3\bar{1}1]$ puts dislocations 2 and 6 out of contrast. Using g.b = 0 criteria, dislocation 1 has b = $\frac{1}{6}[2\bar{1}\bar{1}]$ and dislocation 2 has b = $\frac{1}{6}[1\bar{2}1]$. In order to conserve the Burger's vector, a stair-rod dislocation $\frac{1}{6}[110]$ joins the Shockley dislocations and separates the (111) and $(\bar{1}\bar{1}1)$ stacking faults. Fig. 3/38 shows the Shockley partial reactions in detail at this point. The perfect dislocation $\frac{1}{2}[1\bar{1}0]$ on the inclined γ $(11\bar{1})$ plane can dissociate into two Shockleys

thus:-

$$\frac{1}{2}[110] = \frac{1}{6}[2\bar{1}1] + \frac{1}{6}[1\bar{2}\bar{1}].$$

The perfect dislocation 3 is out of contrast in g $[11\bar{1}]$ verifying that b = $\frac{1}{2}[1\bar{1}0]$. The stacking fault on the inclined γ plane is imaged in g $[\bar{1}1\bar{1}]$, while the Shockley $\bar{\gamma}\bar{A}\ \frac{1}{6}[2\bar{1}1]$ is in contrast and $\bar{B}\bar{\gamma}\ \frac{1}{6}[1\bar{2}\bar{1}]$ is out of contrast. The stair-rod $\frac{1}{6}[110]$ is not imaged, presumably due to its short length. Since dislocation 2 has been identified as b = $\frac{1}{6}[1\bar{2}1]$ and dislocation 4 is b = $\frac{1}{3}[111]$ dislocation 7 has b = $\frac{1}{2}[101]$. This is consistent with the lack of contrast exhibited by this dislocation when g = $[\bar{2}02]$ and $[11\bar{1}]$.

Since this loop is interstitial, two Shockley partials are clearing the stacking fault together, one above and one below. Dislocation 1 must be:-

$$\frac{1}{6}[2\bar{1}\bar{1}] = \frac{1}{6}[1\bar{2}1] + \frac{1}{6}[11\bar{2}]$$

while dislocation 2 is:-

$$\frac{1}{6}[1\bar{2}1] = \frac{1}{6}[2\bar{1}\bar{1}] + \frac{1}{6}[\bar{1}\bar{1}2]$$

These two dislocations are only separated by a single atom layer and so will not be resolved individually. When g = $[\bar{3}\bar{1}1]$, g.b for $\frac{1}{6}[1\bar{2}1] = 0$ while that for $\bar{b} = \frac{1}{6}[2\bar{1}\bar{1}] = -1$ and $\frac{1}{6}[\bar{1}\bar{1}2] = +1$. If the partials $\frac{2\bar{1}\bar{1}}{6} + \frac{\bar{1}\bar{1}2}{6}$ are superimposed, the Burger's vectors will add and cancel out, giving the same contrast as for $\frac{1}{6}[1\bar{2}1]$. Thus for interstitial loops, only one Shockley will effectively be observed removing the Stacking fault, though in reality it will be the sum of two other Shockleys. The dislocation configuration observed in figs 3/38 and 39 is very unusual and presumably arises due to the interaction of the loop on the (111) plane with the inclined loop on the γ $(\bar{1}\bar{1}1)$ plane. Two sets of Shockley partials removing the fault on the δ plane are not normally observed (though it has been observed in quenched Al/Mg by Swart and Kritzinger (1974)) and in

general only the final perfect loop configuration is seen. However, in reactions precipitated by interaction with other loops, intermediate configurations result.

In this particular loop, two sets of partials are removing the fault, the perfect areas of loop being separated by the dislocation $\frac{1}{2}[1\bar{1}0]$, which initially may have been attached at point 8. Similarly, the perfect dislocation 7, $b = \frac{1}{2}[101]$ may have been joined to point 8, generating a complicated reaction at this point. Dislocation 5 which appeared to be involved in the unfaulting process, was found to be a dislocation running from top to bottom of the foil and played no part in the reaction.

The Frank sessile to perfect reaction taking place at point 7 is:-

$$\pm \frac{1}{3}[111] \pm \frac{1}{6}[2\bar{1}\bar{1}] \pm \frac{1}{6}[\bar{1}\bar{1}2] = \pm \frac{1}{2}[101]$$

but that at point 6 is more difficult to identify. Fig. 3/39 shows in detail the partials that can be involved. The Frank partial $\frac{1}{3}[111]$ can dissociate into stair-rod $\frac{1}{6}[011]$ and Shockley $\frac{1}{6}[211]$ on the inclined $(1\bar{1}\bar{1})$ plane. Weak beam micrographs 3/36 and 37 show that the configuration at point 6 resembles that of fig. 3/39. It is also of interest to observe that in $g = [\bar{3}\bar{1}1]$ and $[3\bar{1}1]$ at $z = [011]$ the contrast of dislocations α and β appear different, indicating that two separate Burger's vectors may be involved. Fig. 3/36(d) and 3/37(f) indicate that the dislocation β fig. 3/39(a) is involved in a complex reaction with the $\frac{1}{6}[112]$ and $\frac{1}{6}[110]$ dislocations of the inclined Frank loop on the $(\bar{1}\bar{1}1)$ plane. However, due to contrast difficulties it is impossible to postulate the interaction mechanism.

The possible reactions which can occur where the partial $\frac{1}{6}[2\bar{1}\bar{1}]$ intersects the Frank dislocation $\frac{1}{3}[111]$ at point 6, have been schematically drawn in fig. 3/39 (a)-(d). The Frank partial surrounding the stacking fault on the (111) plane can dissociate by the following reaction:-

$$\frac{a}{3}[111] = \frac{a}{6}[011] + \frac{a}{6}[211]$$

the stair-rod $\frac{a}{6}[011]$ at the intersection of the (111) and $(1\bar{1}\bar{1})$ planes, and the Shockley $\frac{a}{6}[211]$ gliding on the inclined $(1\bar{1}\bar{1})$ plane. Diagram (a) shows what happens when the Shockley $\frac{a}{6}[2\bar{1}\bar{1}]$ clearing the (111) stacking fault, does not intersect the Frank dislocation until point y. The Shockley $\frac{1}{6}[2\bar{1}\bar{1}]$ runs alongside the stair-rod $\frac{1}{6}[011]$, but does not react with it. The resultant dislocation β is:-

$$\frac{1}{6}[211] - \frac{1}{6}[011] - \frac{1}{6}[211] = \frac{1}{2}[0\bar{1}\bar{1}],$$

which is the form of dislocation expected when a Shockley dislocation removes a stacking fault.

Fig. (B) shows basically the same reaction, but with dislocation $\frac{1}{6}[2\bar{1}\bar{1}]$ reacting with $\frac{1}{6}[011]$ at point x, resulting in a Frank dislocation $\frac{1}{3}[1\bar{1}\bar{1}]$ along segment α. Thus

$$\frac{1}{6}[2\bar{1}\bar{1}] - \frac{1}{6}[011] = \frac{1}{3}[1\bar{1}\bar{1}]$$

with the Frank partial reacting with the Shockley on the $(1\bar{1}\bar{1})$ plane to form $\frac{1}{2}[0\bar{1}\bar{1}]$. It follows that

$$\frac{1}{3}[1\bar{1}\bar{1}] - \frac{1}{6}[211] = \frac{1}{2}[0\bar{1}\bar{1}].$$

However, it is energetically favourable for the Frank partial $\frac{1}{3}[1\bar{1}\bar{1}]$ to dissociate into a stair-rod and Shockley partial on the (111) plane,

e.g. $$\frac{1}{3}[1\bar{1}\bar{1}] = \frac{1}{6}[2\bar{1}\bar{1}] + \frac{1}{6}[0\bar{1}\bar{1}].$$

Configuration (d) is that observed in the weak beam micrographs. None of the micrographs show any evidence of the dissociation

$$\frac{1}{3}[1\bar{1}\bar{1}] = \frac{1}{6}[2\bar{1}\bar{1}] + \frac{1}{6}[0\bar{1}\bar{1}].$$

In a <111> diffraction vector, the stacking fault contrast on the (111) plane would be clearly visible. It appears that fig. 3/39(c) is not applicable as an explanation.

In general, a Frank partial will dissociate to lower the dislocation energy and the absence of this indicates that dislocation α may not be

an undissociated Frank partial. It is impossible to determine from the micrographs, whether the partial is $\frac{1}{6}[2\bar{1}\bar{1}]$ or $\frac{1}{3}[1\bar{1}\bar{1}]$ since almost identical g.b products are obtained. The method normally used to distinguish these two dislocations does not work in this case since for a $[0\bar{1}1]$ line direction g.b $\wedge$ U is identical. Energetically the reaction $\frac{1}{6}[2\bar{1}\bar{1}] - \frac{1}{6}[011] = \frac{1}{3}[1\bar{1}\bar{1}]$ is not favourable according to Frank's criteria. In units of $^{36}/a_o^2$ (a_o = lattice parameter), the energies are:- $\frac{1}{6}[2\bar{1}\bar{1}]$ 6, $\frac{1}{6}[011]$ 2, $\frac{1}{3}[1\bar{1}\bar{1}]$ 12. It seems that diagram (a) represents the true reaction and indeed (d) the experimentally observed reaction is consistent with this hypothesis since the stair-rod is difficult to image, even under good weak beam conditions. The theoretical visibility for this dislocation reaction has been computed and it is clear from the micrographs that experimental agreement is consistent with theory except for the perfect dislocation $\frac{1}{2}[0\bar{1}\bar{1}]$at z = [011]. The intensity of contrast in this case is greater than expected, especially when compared to diffraction conditions g $[3\bar{1}1]$ z [011], which gives complete reversal of contrast for dislocations α and β. These two micrographs have g.b = g.b $\wedge$ U = 0, which suggests that no difference should be observed for dislocation β.

3.16 Transformation of a Frank Loop to a Perfect Loop by a Single Set of Partials

The Frank loop reaction discussed has by a process of glide and climb interacted with another loop and the foil surface. This nucleation process, by no means uncommon at high loop densities cannot occur when the loop is isolated.

Fig. 3/40 shows a Frank loop on the (111) plane, which has partially unfaulted by the action of one set of partials, leaving behind a perfect dislocation. The loop can be seen to be complete. The <112> edges of this loop have developed because the specimen has been annealed at elevated temperature after the loops had grown. Since the loop is complete, the

clearing Shockleys must have originated on the (111) plane and reference to table 5 indicates that the resultant perfect loops have $b = \frac{1}{2}[011]$, $\frac{1}{2}[110]$, or $\frac{1}{2}[101]$. Contrast analysis shows that the perfect dislocation has $b = \pm \frac{1}{2}[011]$.

The dislocation at W fig. 3/41 has line direction $[1\bar{1}0]$ indicating that the Frank dislocation may dissociate with the glissile Shockley on the inclined γ plane. The dislocation reaction observed is:-

$$\frac{1}{3}[\bar{1}\bar{1}\bar{1}] = \frac{1}{6}[\bar{1}\bar{1}0] + \frac{1}{6}[\bar{1}\bar{1}\bar{2}]$$

The perfect dislocation at point y can split into two Shockleys, thus:-

$$\frac{1}{2}[011] = D\gamma + \gamma B$$
$$\frac{1}{2}[011] = D\alpha + \alpha B$$

on the inclined α and γ {111} planes. Fig. 3/40 shows partials imaged, with the layer of stacking fault between them out of contrast. The beam normal $\bar{z}$ in this case is near [110], so that plane α $(\bar{1}1\bar{1})$ is edge on. Any dissociation on this plane could not be observed. The two dislocations observed at y must be $\frac{1}{6}[112]$ and $\frac{1}{6}[\bar{1}21]$. Both are visible when g = $[\bar{1}13]$ and invisible when g = $[\bar{1}\bar{1}1]$, in agreement with theoretical visibility criteria.

The perfect dislocation $\frac{1}{2}[0\bar{1}\bar{1}]$ can also split into partials at point z. As the dissociation is only observable when z = [101], the Shockley partials must lie on the $(\bar{1}1\bar{1})$ plane. The reaction involved in this case was

$$\frac{1}{2}[0\bar{1}\bar{1}] = \frac{1}{6}[1\bar{1}\bar{2}] + \frac{1}{6}[\bar{1}\bar{2}\bar{1}]$$

with a low energy stacking fault formed when the outer partial was $\frac{1}{6}[\bar{1}\bar{2}\bar{1}]$. Both partials have been imaged in g $[\bar{1}31]$, z = [101] fig. 3/40(d), while only the outer partial $\frac{1}{6}[\bar{1}\bar{2}\bar{1}]$ was imaged when g = $[13\bar{1}]$, z = [101], fig. 3/40(c).

Since only one dislocation is effectively visible at point x, the Shockleys can be assumed to be close together, giving a contrast equivalent

to the addition of both partials. Experimental results suggest that the Burger's vector of the dislocation removing the stacking fault is $\frac{1}{6}[\bar{2}11]$, which is the addition of $\frac{1}{6}[\bar{1}2\bar{1}] + \frac{1}{6}[\bar{1}\bar{1}2]$, fig. 3/40(b). The structure of the dislocation at point x indicates that it is being pinned, presumably by impurities.

3.17 Conclusion

Irradiation of thin foils of copper aluminium alloys has been observed under specific conditions to nucleate large interstitial Frank loops, of irregular shape, whose sides were aligned along <110>, <112>, <123> and <532> directions. These defects have been imaged in <113> reflections at <110> beam directions, to enable both partials to be resolved. The observations were then compared with the results of convergent beam image calculations.

While Frank dissociation was observed when the loop sides were aligned along <110>, no such dissociation was apparent, for annealed loops with loop sides along <112> or <123> directions. The separation of the two partials tended to vary along the length of a side in the higher alloys, in part as a result of the presence of nearby loops, dislocations on surfaces, but mainly as a result of solute impedance. For these reasons, the observed separations measured for the alloys Cu 10% Al and Cu 16% Al varied to a large extent.

The weak beam technique was also used, to image the reactions that occur when Shockley partials shear the Frank loop to a perfect loop. While the results of Frank dissociation separation remain inconclusive, the main objective of imaging the dissociation along <110> directions was achieved.

CHAPTER 4

Image Analysis of Rhombohedral Shaped Loops Formed During Electron Irradiation of Copper Aluminium Alloys

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4.1 Introduction

Nucleation and growth of dislocation loops was observed over a wide range of temperatures in several copper aluminium alloys. At room temperature, a very high loop density $\simeq 10^{17}$ cm^{-3} was observed, but these loops did not grow into loops large enough to be resolved except as 'black dots' under kinematical conditions, or for loops close to the surface imaged under dynamical conditions, as 'black-white' contrast.

As the temperature of the foil was raised, the loop density decreased and the loop size increased. The most common form of loop observed in the range of alloys Cu 1% Al to Cu 16% Al in slow grown crystals was found to be of perfect nature, with $\frac{a}{2}$ <110> Burgers vector and having rhombohedral shape. Irradiation conditions were chosen such that a low density of these loops grew in foils $\simeq 2200$ Å in thickness, to a size of about 1500 Å. Experimental evidence obtained for this thesis suggests that the stress fields of nearby loops or surfaces (Chapter 3) effects the ultimate geometry. Loops of diameter greater than 1500 Å change their shape by glide and climb mechanisms, thus making a determination of their habit place difficult.

Similar loops have been observed in quenched aluminium alloys by Hirsch (1958), Kuhlmann-Wilsdorf (1960), Embury (1963), Makin (1963), Eikum (1963), Das (1964); in quenched copper alloys by Eikum (1963), in irradiated platinum by Ruedle (1962) and in Aluminium alloys by Westmacott (1964), Vigelholm (1965). The loops in these quenched metals were analysed as being of vacancy nature, but in the irradiated metals, both vacancy and interstitial defects were found.

The final shape and crystallography of these defect aggregates are of considerable interest and theoretical investigations have been carried out by Bullough (1964) Bacon (1966) and (1970), to find the lowest energy form of the rhombus loop. The calculations of Bullough (1964) and Bacon (1966) used an isotropic elastic continuum model which predicted a shallow

minimum at an orientation close to {012}. Bacon (1970) questioned the assumption of isotropy in the previous calculations and the conclusions drawn from them. Bacon, using a solution by Willis (1970) for the distortion field produced by a finite straight dislocation segment in an arbitrary anisotropic body derived an expression for the anisotropic elastic energy of a rhombus shaped dislocation loop. He studied the energy variation of a rhombus loop constrained to glide on a {111} prism in aluminium and copper and compared the results with the previous isotropic calculations.

4.2 Burgers Vector Determination of Rhombus Loops

The analysis was based on the results of the kinematical and dynamical theories of electron diffraction by Hirsch et al. (1965). Using the $g.b = 0$ criterion, an unambiguous determination of the direction of $\bar{b}$ in general requires that two operating reflections are obtained for which the dislocation is in extinction, although if the family of directions for $\bar{b}$ are known, a unique answer may be obtained with a single reflection. In the experiments discussed here, <111>, <200>, <220> and <113> reflections were used and several ± g pairs were taken so that the loop nature could be positively identified.

Fig. 4/1 shows a series of micrographs taken in different diffraction vectors. Some loops have the characteristic rhombus or square shape, depending on the projection, while others appear nearly 'edge on'. As the foil normal was cut along [111], it was easy to tilt to the three <111> diffraction vectors at z <211>, though it was not always possible to tilt to <110>. It is clear, that care must be exercized when examining loops in $g.b = 0$ contrast, as large components of $g.b \wedge U$ tend to image the loops in good contrast.

In the initial determination of the Burger's vectors, values of $g.b \wedge U$ were computed whenever $g.b = 0$, in order to avoid ambiguity. Table 6(A) shows the contrast observed experimentally for loops 1 to 7

Table 6 (A)

Rhombus Loop Invisibility

The Burgers Vector can be obtained by considering only g $\bar{1}1\bar{1}$, $1\bar{1}\bar{1}$ and $\bar{2}00$.

Loop No.	g_7 $\bar{1}1\bar{3}$	g_1 $\bar{1}11$	g_2 $1\bar{1}\bar{1}$	g_3 $\bar{2}00$	g_4 $\bar{2}02$	g_5 $\bar{1}\bar{1}1$	g_6 $0\bar{2}2$
1	I	0	I	I	I	I	I
2	I	0	0	I	I	I	I
3	I	I	0	I	0	0	I
4	0	I	I	I	I	0	I
6	I	0	I	0	I	0	0
7	I	I	0	0	I	I	I

For loop identification refer micrographs 0 = out of contrast

I = in contrast

Table 6 (B)

Results of contrast analysis of electron produced 'rhombus' loops:-

all loops interstitial

Loop	Possible $\bar{b}$	Habit	Image Larger (g.b)s > 0	$\bar{b}$	- Beam Direction $\bar{z}$	$\bar{z}.\bar{b}$	Nature
1	$\pm\frac{a}{2}[10\bar{1}]$	$(10\bar{1})$	$(0\bar{1}1)$	$\frac{a}{2}[\bar{1}01]$	[233]	> 0	int.
2	$\pm\frac{a}{2}[110]$	(110)	$(10\bar{1})$	$\frac{a}{2}[110]$	[121]	> 0	int.
3	$\pm\frac{a}{2}[101]$	(101)	$(0\bar{1}1)$	$\frac{a}{2}[101]$	[233]	> 0	int.
4	$\pm\frac{a}{2}[1\bar{1}0]$	$(1\bar{1}0)$	$(\bar{1}01)$	$\frac{a}{2}[\bar{1}10]$	[121]	> 0	int.
6	$\pm\frac{a}{2}[011]$	(011)	$(\bar{1}01)$	$\frac{a}{2}[011]$	[121]	> 0	int.
7	$\pm\frac{a}{2}[01\bar{1}]$	$(01\bar{1})$	$(10\bar{1})$	$\frac{a}{2}[01\bar{1}]$	[121]	> 0	int.

in figs 4/1 and 4/2. It is clear that the absence of stacking fault fringes in the parallelogram loops rules out $\frac{a}{3}$ <111> Burgers vectors, while only three different Burgers reactors would be observed if b = a <100>. Two extinctions of all loops in fig. 4/1 were observed, with the exception of loop 4. Considering loop 3 for example; when g = $[1\bar{1}\bar{1}]$ residual contrast was observed. Similarly in g = $[20\bar{2}]$. Therefore since $b = g_1 \wedge g_2$, the Burgers vector of this loop is $\pm \frac{a}{2}[101]$. Similarly the Burger's vector of loop 2 was determined to be $\pm \frac{a}{2}[110]$, because g.b = 0 for both $[1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}]$ reflections. The same methods were applied to the other loops, where it was found that $b = \pm \frac{a}{2}$ <110>.

4.3 Experiments to determine the Nature of Rhombus Loops

Having determined the magnitude of $\bar{b}$, the sense and the nature of pure edge loops can be determined by noting the shift in the image position on changing the sign of (g.b)s. In the case of non edge loops, some knowledge of $\bar{n}$ (the vector defining the upward loop normal) is necessary. For rectilinear loops, it is possible to measure the loop normal by measuring the projected directions of the sides at two or more foil orientations using a stereographic plotting procedure.

Fig. 4/3 shows the stereographic projection used to find the normal to loop plane 2, which was chosen because its sides were in good contrast and not curved. In order to obtain accurate results, the diffraction vectors were aligned on the prints using the known directions of the 'edge-on' Frank loop 5 with $b = \pm \frac{a}{3}[\bar{1}1\bar{1}]$ and a direction along $u = [\bar{1}01]$. Beam normals were chosen to lie exactly along low index directions and were adjusted so that other low index reflections were not satisfied. For this particular analysis, beam directions A, B and C were chosen fig. 4/3 having normals [032], [323] and [233] respectively. The sides of loop 2 were labelled $\alpha 1$ and $\alpha 2$ to avoid confusion. The angle between $\alpha 1$, $\alpha 2$ and the diffraction vector was measured and the sense of rotation obtained by noting the direction of other low index orientations from

the diffraction pattern. Curves were drawn on the projection at 90^{o} to the A, B, C zone axes which represented directions lying in the A, B, C planes.

Considering beam direction [323], projections BUα1 and BUα2 were plotted. Since the loop was in projection, the exact direction of the sides must lie on a line joining B and BUα1 or B and BUα2. When micrographs were taken at other beam normals, the intersection of these directions gave the exact line direction of the loop edges. Thus $U\alpha 1 = [2\bar{3}\bar{5}]$ and $U\alpha 2 = [2\bar{3}5]$. When the cross product of these sides was taken, or lines at ninety degrees to $U\alpha 1$ and $U\alpha 2$ plotted on the stereogram, the intersection was found to be [320]. Thus the normal for loop 2 is [320], which lies 11^{o} from its Burgers vector $\frac{a}{2}[110]$. The same method was used to find orientations of the other loops and the result is shown in fig. 4/4. From this diagram, the crystallography of these irradiation produced parallelogram loops becomes clear. In general, they lie on planes $5 - 10^{o}$ from {110} planes, with their sides along <211>, <532> or <312> directions, which lie in the loop plane. The Burgers vector of these loops lie along the <110> direction nearest the loop normal. Thus, when $\bar{b}$ has been calculated, a first estimate of the loop normal can be obtained.

These loops are prismatic in character and referring to fig. 4/3, loop2 which lies on the (320) plane has sides along $[2\bar{3}\bar{5}]$, $[2\bar{3}5]$ and a Burger's vector along [110]. The $[2\bar{3}\bar{5}]$ side lies on the $(1\bar{1}1)$ slip plane and the $[2\bar{3}5]$ side on the $(1\bar{1}\bar{1})$ plane. Since the Burgers vector of the loop $\frac{a}{2}[110]$ is common to $(1\bar{1}\bar{1})$ and $(1\bar{1}1)$ slip planes, the loop is capable of conservative glide along [110] without change of shape as proposed by Makin (1963).

The (g.b)s experiments were carried out by reversing the sign of g, keeping S_g positive and using the formal analysis of Mazey (1962). In the case of non-edge loops a knowledge of n is necessary, but provided the foil orientation is such that $\bar{b}$ and $\bar{n}$ fall within the 'safe' region as

defined by $\bar{n}.\bar{z} > 0$, $\bar{n}.\bar{b} > 0$, where $\bar{z}$ is the upward beam normal, they can be treated in the same manner as pure edge loops, Maher (1970). For F.C.C. metals, Makin (1963) proposed that loops nucleate on {111} planes with $b = \frac{a}{3}\langle 111\rangle$, then subsequently shear to $\frac{a}{2}\langle 110\rangle$. The maximum angle between $\bar{b}$ and $\bar{n}$ is therefore 35^{o} and thus if the angle between $\bar{b}$ and $\bar{z}$ is $<55^{o}$ the foil orientation is safe for such loops. A formal stereographic analysis is not required every time the loop sense is to be examined, if the above boundary conditions are satisfied. In this analysis, both $\bar{b}$ and $\bar{n}$ are accurately known.

Fig. 4/2 shows the inside-outside contrast phenomenon when imaged under $\pm$ g $[20\bar{2}]$ and $\pm$ g $[02\bar{2}]$. The convention used in this thesis is that interstitial loops are imaged in outside contrast when $(g.b)s > 0$ and $z.b > 0$. Outside contrast for loops 2 and 7 occurs when $g = [20\bar{2}]$, giving $\bar{b} = \frac{a}{2}[110]$ and $\frac{a}{2}[01\bar{1}]$. As the beam direction $\bar{z} \simeq [121]$, $\bar{b}.\bar{z} > 0$ and the loop sense is interstitial. Loops 4 and 6 have inside contrast when $g = [20\bar{2}]$, but outside contrast in $g = [\bar{2}02]$. The inclination of these loops differ from 2 and 7 however, and when the appropriate Burger's vector was ascribed i.e. $\frac{a}{2}[\bar{1}10]$, $\frac{a}{2}[011]$, $\bar{b}.\bar{z}$ for both loops > 0. All the loops examined in the microscope turned out to be interstitial as expected.

In order to examine the nature of loops growing, in a dynamic H.V.E.M. experiment without interrupting the radiation to take micrographs, the position of the [111] and <110> beam directions were established from the diffraction pattern to give an unambiguous determination of $\bar{g}$ prior to the experiment. The loop normals and hence the Burger's vectors can be established by aligning a tetrahedron along the diffraction vector and considering the projections of the loops at the beam direction concerned. Fig. 4/5 shows with the aid of a Thomson tetrahedron in projection, the shapes of the rhombus loops at two different beam directions. The Greek letters indicate the {111} planes on which the loop sides are aligned.

Fig. 4/6(a) illustrates schematically the prismatic character of the loop 2, lying on the (320) plane which was analysed in this chapter by the stereographic method. The Burgers vector $\frac{a}{2}[110]$ is common to the $(\bar{1}1\bar{1})$ and $(1\bar{1}\bar{1})$ planes, which contain respectively the loop sides $[2\bar{3}\bar{5}]$ and $[2\bar{3}5]$. The loop can lower its energy by allowing each side to dissociate into Shockley partials, which for loop 2 are:-

$$\frac{a}{2}[110] = \frac{a}{6}[121] + \frac{a}{6}[21\bar{1}] \text{ on } (\bar{1}1\bar{1}) \text{ plane}$$

and

$$\frac{a}{2}[110] = \frac{a}{6}[211] + \frac{a}{6}[12\bar{1}] \text{ on } (1\bar{1}\bar{1}) \text{ plane.}$$

These reactions have been observed using the 'weak beam' method, the results of which are presented in this chapter. It seems likely that this dissociation stabilizes these loops in the rhombus configuration.

Fig. 4/6(b) shows the atom positions on the (001) face of an F.C.C. structure for a rhombus loop. Dots represent atoms on the face and crosses the atoms displaced perpendicular to the paper by half a lattice spacing. It is not possible on any particular $(\bar{1}20)$ plane to find a Burger's vector which will enable one plane to be removed and the lattice to reunite, without leaving a stacking fault. If three adjacent $(\bar{1}20)$ planes are considered however then it is clear that when these are removed the lattice can re-unite with a Burgers vector of $\frac{a}{2}[\bar{1}10]$ leaving no stacking fault.

4.4 Geometrical Formation of {320} plane Rhombus Loops

It has not been possible to deduce from the present experiments, an unambiguous mechanism of rhombus loop formation. Though condensation of point defects could occur directly on {110} planes forming loops which then rotate to an {320} orientation, there is no evidence to substantiate this hypothesis. Weak beam micrographs of loops $\simeq 120$ Å diameter were imaged and these were positively identified as having $b = \frac{a}{2}\langle 110\rangle$. Below this size, defects can only be examined using 'black white' contrast. However, in H.V.E.M. irradiated foils loops only form at depths in excess

of 350 Å at room temperature. The number of loops which did exhibit 'black white' contrast appeared to be a small percentage of the total loops present; the loops in the thicker regions appearing only as black dots. However, some data accumulated from a number of experiments on small loops 30 Å - 100 Å in size in specimens of Cu 5% Al and Cu 16% Al alloys irradiated at room temperature indicate that the large majority of loops had $b = \frac{a}{2}\langle 110\rangle$ down to sizes of $\simeq$ 40 Å. A possible explanation of these results is that point defects agglomerate onto the four {111} planes to form Frank loops, which then shear by the passage of Shockley partials when the loops are smaller than 40 Å in diameter.

Fig. 4/7 illustrates the method by which rhombus loops may form from Frank loops as proposed by Eikum (1963). It was assumed that the point defects aggregate on the (111) plane to form a triangular defect with $b = \frac{a}{3}[111]$. The activation energy required to nucleate the Shockley partials to remove the stacking fault can be supplied by thermal stresses, surface contamination stresses, bending of foil, or in the case of copper aluminium alloys a solute size effect stress introduced when aluminium was added to copper. A gradual transformation of Frank loops to perfect loops has been observed in these alloys as the solute content was increased, while keeping constant irradiation conditions for each specimen.

Once the stacking fault has been removed the Burgers vector is transformed to $b = \frac{a}{2}[110]$ but with the loop sides along $[\bar{1}01]$, $[0\bar{1}1]$ and $[1\bar{1}0]$. It is energetically favourable for the loop sides along $[\bar{1}01]$ and $[0\bar{1}1]$ to dissociate into Shockley partials as shown in fig. 4/7(b), though in the case of loops smaller than 40 Å the partial separation will be smaller than that in larger loops dissociated under equilibrium conditions. With a Burgers vector along [110], the loop sides along $[\bar{1}01]$ or $[0\bar{1}1]$ are of mixed edge or screw character and can glide in the $(\bar{1}1\bar{1})$ or $(1\bar{1}\bar{1})$ planes. The dislocation along the $[1\bar{1}0]$ direction is pure edge, so that if the loop redistributed its defects to eliminate this side, a

diamond shape could result. In the case of radiation induced damage the pure edge side can by a climb and glide mechanism form a rhombus shape. Fig. 4/7(c) shows the final configuration achieved, with stair-rods $\bar{\alpha}\bar{\beta}$ and $^{\alpha\beta}/_{DC}$ at the intersection of the stacking fault planes.

Reference to fig. 4/8 illustrates how the final loop orientation is achieved. The loop sides $[0\bar{1}1]$ and $[\bar{1}01]$ are shown before gliding takes place. For a loop normal [110] to occur, the loop sides must rotate to $[1\bar{1}2]$ and $[\bar{1}12]$ directions. Direction (A) shows the path followed when equal rotation of loop sides takes place. A final orientation of (210) and (320) results if loop rotation takes place around the [001] axis and the loop side along $[1\bar{1}2]$ rotates to $[\bar{1}23]$ or $[2\bar{3}5]$. Similarly the side parallel to the $[\bar{1}12]$ direction can rotate to $[\bar{1}23]$ or $[\bar{2}35]$ directions. Path B does not seem very likely, since the $[0\bar{1}1]$ side at first rotates through $[2\bar{3}5]$ to reach orientation $[1\bar{1}2]$ ($\bar{n}$ = 110) and then reverses back to finally align itself along $[2\bar{3}5]$. A more likely path is that of c, in which side $[0\bar{1}1]$ rotates to $[2\bar{3}5]$ and then stops, while side $[\bar{1}01]$ continues to reach $[\bar{2}35]$. Whether the final loop normal is along [210] at [120] presumably depends on the speed of each rotating side. If side $[\bar{1}01]$ reaches $[\bar{2}35]$ before $[0\bar{1}1]$ reaches $[2\bar{3}5]$, the final orientation will be (320), however if side $[0\bar{1}1]$ reaches $[3\bar{1}5]$ before $[\bar{1}01]$ reaches $[\bar{3}25]$, then the loop orientation will be (230). The final orientation is likely to depend on foil stresses and on solute pinning of the gliding dislocations. Final loop orientations measured by stereographic projections have been observed along path D, indicating that unequal rotation takes place.

Makin (1963) observed that in quenched Al 1% Mg specimens, the majority of loops lay very near {210} planes. In the analysis performed for this thesis, loop normals were observed near {320}, an angle difference of 7^{o}. Since it is likely that impurities pin the dislocations and that glide motion is impeded as the stacking fault energy is reduced, the final

loop orientations will depend to a certain extent on the alloy concentration. The specimens which Makin used had a much smaller dissociation and thus less restriction on glide motion, so that the angle of rotation from the (110) plane was $\simeq 18^{o}$. Thus it seems that rhombus loops in pure materials rotate to a much greater extent than in concentrated alloys. In these latter materials it appears that there is no well defined path for rotation since foil stresses and pinning stresses tend to vary from specimen to specimen. Though the mechanism outlined for the transformation from Frank to rhombus loop has assumed a triangular Frank loop, the method is equally applicable to polygonal Frank loops.

A prismatic loop has its smallest line length at the pure edge orientation, but since opposite sides interact with each other, the equilibrium configuration can be several degrees from the pure edge position. The final orientation is a function of loop size, since the interaction between loop sides decreases as the loop size increases. Since opposite sides of loops have opposing Burgers vectors, shear stresses acting on them cause movement in opposite directions on their glide allowing the loop to rotate away from its equilibrium orientation increasing the loop energy until the rate of energy increase balances the shear stresses. Thus a new equilibrium position can be reached.

Bacon (1970) and Bullough (1964) in their calculations assumed that the loop sides remain straight and lie in their {111} glide planes throughout the rotation. The results of these calculations indicated that no energy minimum between <111> and <110> orientations could prevent the initial rotation, but when rotation about the <100> axis was considered, an energy minimum occurred, whose position appeared to depend on the loop size and Poisson's ratio. Anisotropic elasticity calculations deepened the minimum expected and also predicted a sharply decreasing energy variation even for the smallest loops, in contrast to isotropic calculations which predicted a minimum between [111] and [110] directions.

Aluminium and copper were chosen as representative materials on which to perform calculations, because of their differences in isotropy. The anisotropy factor for copper being 3.21 as compared to 1.22 for aluminium. The main differences in these results is that for copper the minimum is flatter and closer to the (001) orientation. This result contrasts with the conclusion drawn from this thesis, that loops in copper having a much lower stacking fault energy than aluminium, would be expected to rotate to a lesser extent from the (110) plane.

Figs 4/9 plotted by Kosel (1975) from data by Bullough and Foreman (1964) show loop energies as a function of loop size and orientation for rotation about the <100> major axis fig. 4/9. The calculations assume that the resolved shear stress is equal on all sides of the loop. The zero stress equilibrium orientation of a loop is farther away from pure edge for a smaller loop. A given stress will produce different orientations for different loop sizes and a loop which grows under constant stress should change its orientation as it grows. Calculations suggest that the initial rotation about the <110> axis occurs very easily as the loop energy can reduce rapidly with rotation.

Fig. 4/10 illustrates the extent to which loops can change shape as they increase in size. A graph of the angle between the acute sides of loop β has been plotted as a function of the loop diameter in fig. 4/11. When the loop was small, the shape appeared regular and the angle between the sides measured as $\simeq 90^{\circ}$. As the loop increased in size, the loop side curvature increased and the angle between them decreased, indicative that the loop was changing orientation as its size increased. When the loop diameter approached 2000 Å, irregular growth occurred. Probably as a result of the proximity of foil surfaces. Thus any loop rotation above this diameter is likely to be influenced by surface stresses. Fig. 4/10(b) also shows loops in the 'edge on' configuration whose long diameter is parallel to $[1\bar{1}1]$. Though these loops are in residual contrast in this

diffraction vector, it is possible to observe that as the irradiation continues and the loops increase in size, they rotate away from the edge configuration by about 10^{o}. This rotation can be seen in fig. 4/10(d).

The presence of shear stresses which rotate the loops cause the loop sides to bow out on their glide planes, as shown in fig. 4/10. This curvature of the loop sides is due to glide, rather than climb, since observations of loop sides in planes parallel to the viewing direction are straight, whereas those sides lying on inclined planes are curved. Curvature due to climb would be visible in the images of loop sides lying in 'edge on' {111} planes. It was not found possible to relate with any degree of confidence loop orientation with a given side length, since loops of the same size tended to exhibit different curvatures of sides and different angles of rotation.

Explanations of this phenomenon probably lie in the fact that impurities or foil stresses (which differ from area to area) may restrict the motion of the dislocations. However, one important parameter that should be considered is the influence of the specimen surfaces, which according to Groves (1970) can influence and modify the final loop orientation. In order to study this effect in detail however 'weak beam' stereopairs are needed, to measure the orientation of loops at known depths in the foil.

Fig. 4/12 illustrates the development of additional sides, when the loop size becomes comparable with the foil thickness. At small loop sizes, the regular rhombic shape can be observed, but as the loop diameter increases, additional loop edges may develop along the $[2\bar{1}\bar{1}]$ direction fig. (B). As the loop corners grow towards the foil surfaces additional edges may develop to give the appearance of fig. (C). Loop β fig. 4/10(b) illustrates this behaviour. At these loop sizes, the diameter along the $[0\bar{1}1]$ direction increases, while the other remains constant. Many rhombus loops nucleate three or more additional edges, whose sides on the {111}

planes are stabilised by dissociation. As the loop corner grows nearer the surface, the surface acts as a dominant sink for interstitials and anisotropic growth occurs.

At very large loop sizes, additional edges may develop on a third {111} plane, as shown in fig. 4/13. This is again illustrated by loop β in fig. 4/10(d), which is now so irregular that the original rhombus shape is hardly observable. The irregular edges have now become a smooth curved dislocation line, as a result of surface stress effects. If this edge does lie on a third {111} plane, it can only move by climb and the curved shape suggests that it has a very high jog density. The irregularities which occur during rhombus loop growth do not move along the loop sides in a regular manner, which would be expected if these steps were 'superjogs' whose passage was responsible for loop growth.

4.5 Interactions Between Rhombus Loops

The question of interactive forces between loops has received theoretical attention by Foreman (1962), who calculated the interaction energy for a pair of like parallel loops with their centres joined by the vector (r,θ) in polar coordinates. This energy has its origin in the overlap of two elastic strain fields and since these are very anisotropic, the force may be either attractive or repulsive according to the relative position. In plotting contours of constant interaction energy for the case of $\bar{b}$ parallel to $\bar{n}$ ($\bar{n}$ = loop normal), they found that for $\theta = 0$ when the loops were above each other, the energy was positive and the loops repelled. However, for $\theta = \pi/2$, the loops approach the same plane and the force was found to be attractive. Between $\theta = 0$ and $\pi/2$, the interaction energy changed from being positive to negative. When the loops do attract each other, the energy in each case falls off as r^{-3} and becomes negligible when $r > 5$ loop diameters. Thus it follows, that if loops are able to move by glide, climb or pipe diffusion, there is a good chance that they may join up to form larger loops, or in some cases special

arrays of loops.

Fig. 4/14(a) illustrates how loops having the same Burgers vector of $b = \pm \frac{a}{2}[101]$ and sides in the $(1\bar{1}\bar{1})$ and $(\bar{1}\bar{1}1)$ planes can interact. When the loops interact so that their strain fields overlap, it is possible for the loops to amalgamate. If the dislocations on the $(1\bar{1}\bar{1})$ planes approach each other, these sides will eliminate each other as they have opposite Burgers vectors. This was the most frequent form of loop interaction observed in the experiments performed and typical examples can be seen in fig. 4/15. Interactions between similar loops have been labelled (A). In fig. (b) loop A1 indicates that the forces exerted by these loops on one another can be considerable as a distinct step can be observed in the final loop configuration. These loops have $\bar{b} = \bar{n} = \frac{a}{2}[\bar{1}01]$.

Loops having disimilar Burgers vectors can interact and agglomerate when one side of each loop lies in the same glide plane. If diagram 4/14(b) is considered, both loops $b = \frac{a}{2}[101]$ and $b = \frac{a}{2}[0\bar{1}1]$ have a side common to $(1\bar{1}\bar{1})$. The interaction takes place between dislocations α and β, and generally has been observed to take place at the corners, where it is easier for the loops to join up. However, these interactions denoted by B on fig. 4/15 are not as commonly observed as the A type interactions. The reaction which occurs when the loops in fig. (b) intersect is

$$\frac{1}{2}[01\bar{1}] + \frac{1}{2}[101] = \frac{1}{2}[110].$$

In fig. 4/15 loops B1 and B2 illustrate two reactions:-

$$\text{loop B1} \quad \frac{a}{2}[011] + \frac{a}{2}[10\bar{1}] = \frac{a}{2}[110]$$

$$\text{loop B2} \quad \frac{a}{2}[011] + \frac{a}{2}[1\bar{1}0] = \frac{a}{2}[101]$$

Since $g = [1\bar{1}\bar{1}]$ neither dislocations $\frac{a}{2}[110]$ nor $\frac{a}{2}[101]$ are in contrast.

A third interaction is possible, but has not been observed during the experimental observations. This is shown in figs. 4/14(c) and 4/16,

in which none of the loop sides are in the same glide plane. Loops with $b = \frac{1}{2}[0\bar{1}1]$ and $\frac{1}{2}[011]$ can dissociate onto the (111) and $(\bar{1}\bar{1}1)$ planes such that

$$\frac{1}{2}[0\bar{1}1] = \frac{1}{6}[\bar{1}\bar{1}2] + \frac{1}{6}[1\bar{2}1]$$

and

$$\frac{1}{2}[011] = \frac{1}{6}[\bar{1}21] + \frac{1}{6}[112]$$

This reaction is shown in fig. 4/16(A). If the loops approach close enough, so that the leading partials join up, a 'Lomer-Cottrell' lock will be formed.

Thus

$$\frac{1}{6}[1\bar{2}1] + \frac{1}{6}[\bar{1}21] = \frac{1}{6}[002]$$

with a high energy stair-rod at the intersection of the (111) and $(\bar{1}\bar{1}1)$ planes.

The interactions discussed in this chapter appear to depend critically on the loop density and the size of the loops. At temperatures in excess of $\triangleq 220^{\circ}C$ loop amalgamation was rarely observed due to the low density and rapid growth of the loops. When loops at these temperatures did approach each other, they either slipped to the surface or formed a dislocation tangle. Many attempts at void formation in the H.V.E.M. have been frustrated by the choice of inadequate foil thickness which allows dislocation loss by slippage to the surface. The minimum density required in order for loops to agglomerate has been observed to be in the region of 7×10^{15} loops cm^{-3}, the higher the density the greater the possibility of agglomeration. In foils of thickness 2500 Å the maximum size of loop diameter for interaction to occur was $\triangleq$ 2500 Å and loops of diameter below this appeared to join together successfully to grow in the same way as the original loops. The ideas incorporated in this chapter have been developed further in chapter 7 to explain the very broad size distributions that have been observed.

4.6 Weak Beam Observations of Dissociated Rhombus Loops

The analysis of the crystallography of rhombus shaped loops revealed that these lie near {012} planes, with sides ≃ along <312> directions and have Burgers vectors $b = \frac{a}{2}$ <110>. Various authors have discussed the formation of these loops; Makin and Hudson (1963); Barry and Eyre (1970); Westmacott and Peck (1971) and have concluded that dissociation of the perfect dislocation into Shockley partials tends to restrict movement to the {012} <312> configuration.

Rhombus loops in a Cu 16% Al foil have been imaged using weak beam diffraction conditions figs 3/21 - 3/24 and the Burgers vectors identified by adjusting g.b to equal zero. By this method, loops A, C, N and K were found to have $b = \pm \frac{a}{2}[0\bar{1}1]$, which could then split into two partials of $b_1 = \frac{a}{6}[\bar{1}\bar{1}2]$ and $b_2 = \frac{a}{6}[1\bar{2}1]$ free to glide in the {111} planes. Both partials Cδ and δA were visible when imaged in $g = [0\bar{2}2]$, $\bar{z} = [011]$, while in $g = [20\bar{2}]$ $\bar{z}$ [111] only one partial, Cδ was visible. For loop A this partial was on the outside of the loop in contrast to that for loop N, where it was on the inside. The third {220} diffraction vector, $g = [\bar{2}20]$ z = [111] shows the partial δA on the inside of loop A, while the order of partials was reversed for loop N.

Diagram fig. 3/17 shows a perfect $\frac{a}{2}[0\bar{1}1]$ dislocation and its component partials. The passage of a perfect dislocation $\frac{a}{2}[0\bar{1}1]$ from the bottom to the top of the figure results in the atom originally at (a) being displaced to (c). Motion of the atom along the straight line (a)-(c) involves in the 'hard sphere' model a larger dilatation normal to the slip plane and hence a larger misfit energy than does motion along path (a) to (b) to (c), and so this path is favoured. Thus an intrinsic stacking fault and its associated shear can be produced by the motion of a partial dislocation $\frac{a}{6}[1\bar{2}1]$. The fault is removed to restore the perfect lattice behind the dislocation by the subsequent glide of a partial $\frac{a}{6}[\bar{1}\bar{1}2]$. Application of the Frank criterion $b_1^2 > b_2^2 + b_3^2$ shows that the elastic

strain energy in a crystal is reduced by the dissociation into Shockley partials, but the order of splitting decides whether an intrinsic or extrinsic fault is formed. If in fig. 4/17(a) the partial BC had preceded AB, the intermediate configuration would have been D, which has a large misfit energy.

Fig. 4/17(c) illustrates, that for each Burgers vector $b = \frac{1}{2}\langle 011\rangle$, two loop planes {012} and {021} exist. On this basis, the difference in sequence of the partials of loops A,K and C,N can be explained if it is assumed that these loops lie on planes oppositely inclined to the {011} plane.

Fig. 3/23 shows the contrast when rhombus loops were imaged using $g = \langle 111\rangle$ $\bar{z} = \langle 211\rangle$. At each of these beam directions, one {111} plane is edge on, two are very steeply inclined and the fourth at an angle of 19°. While the stacking fault on the (111) plane can be easily observed those on the inclined planes were difficult to image due to the inclination.

The difference in the angle of projection of loops A,K and C,N can be observed in fig. 3/24 in which $g = [\bar{2}20]$, $z = [113]$. Though the Burgers vector of the loops is $\frac{a}{2}[0\bar{1}1]$, loops A,K appear to be steeply inclined, while C,N have a broad projection. The loop normals associated with $b = \frac{1}{2}[0\bar{1}1]$ are $\bar{n} \triangleq [02\bar{1}]$ and $\bar{n} \triangleq [0\bar{1}2]$. At a beam direction of [113], the angle between $\bar{z}$ and loop normal $[02\bar{1}]$ is 90° while that between $\bar{z}$ and $[0\bar{1}2]$ is $\triangleq 56^{\circ}$. Thus, in comparing the angles of projection, loops C,N lie on the $(0\bar{1}2)$ plane, while loops A,K lie on the $(02\bar{1})$ plane. (A more realistic approximation for Cu 16% Al specimens is that the loop normals lie near {320} planes, rather than the {210} planes assumed in the argument above). Results consistent with this analysis were obtained when loop projections were compared at other beam directions. Thus instead of six different rhombus loops being nucleated, twelve are expected Das (1964), though in general, it is not easy to differentiate each plane

associated with individual Burgers vectors.

Loop B has been identified as having $b = \pm \frac{1}{2}[101]$. This Burgers vector can dissociate according to the reaction:-

$$DA = D\beta + \beta A \text{ and } DA = D\gamma + \gamma A$$

though the partial dislocations are not visible on the β or γ planes due to the steep inclination at the beam directions visited in the experiment. In fig. 3/24, with $g = [\bar{2}20]$ $\bar{z}$ $[113]$ the γ plane is on edge, but the stacking fault on the β plane can be observed as a series of broken lines.

Loop F, with a Burgers vector $b = \frac{1}{2}[10\bar{1}]$ is an interesting example of a rhombus loop whose image suggests that a stair-rod dislocation exists at the intersection of the stacking faults on the {111} planes. Referring to fig. 3/24 again, only the partial $\frac{1}{6}[2\bar{1}\bar{1}]$ is predicted to be in contrast on the (111) plane. The Shockley partial αB on the steeply inclined $(\bar{1}1\bar{1})$ plane is difficult to distinguish due to the fringe contrast from the stacking fault on this plane. The stair-rods associated with a loop of Burgers vector $b = \frac{1}{2}[10\bar{1}]$ are $\alpha\delta$ and $\frac{BC}{\alpha\delta}$, the latter being a high energy stair-rod. It is this dislocation which is likely to be imaged, since stair-rods of the type $\alpha\delta$ are predicted to be out of contrast. However, further evidence in the form of weak beam migrographs is needed, before any positive conclusion can be drawn.

Loops G, I, L, M have been identified as having $b = \frac{a}{2}[1\bar{1}0]$, which can dissociate into partials $B\gamma + \gamma A$ on the $(\bar{1}\bar{1}1)$ plane and $B\delta + \delta A$ on the (111) plane. Two different loop planes $(2\bar{1}0)$ and $(1\bar{2}0)$ have been observed in the micrographs to be associated with this Burgers vector, in a similar manner to loops A, C, N and K. When imaged in $g = [\bar{2}20]$, all the partial dislocations are predicted to be in contrast, though in fig. 3/24, only $\frac{a}{6}[2\bar{1}\bar{1}]$ and $\frac{a}{6}[1\bar{2}1]$ are observed due to the $(\bar{1}\bar{1}1)$ plane being steeply inclined to the beam direction. The stacking faults on $(\bar{1}\bar{1}1)$ and (111) are both predicted and observed to be out of contrast. Fig. 3/22(g) illustrates these loops when imaged in $g = [20\bar{2}]$ $\bar{z} = [343]$

conditions, in which the outer partial $\frac{a}{6}[2\bar{1}\bar{1}]$ on the (111) plane is in contrast. At this direction loops G, M can be observed to have broad projection, while loop L has narrow projection, in agreement with calculated angles between [343] and $[2\bar{1}0]$,$[1\bar{2}0]$ directions of 82^{o} and 114^{o} respectively. Loop L in the near edge configuration has loop normal $[2\bar{1}0]$ while loops G and M lie on $(1\bar{2}0)$ planes.

The remaining loop in this set of micrographs is J with $b = \frac{a}{2}[011]$. Though dissociation occurs on the γ and α planes, no partials were observed due to the inclination of the stacking faults. In fig. 3/24, the stacking fault on the $(\bar{1}\bar{1}1)$ plane is on edge, while that on $(\bar{1}1\bar{1})$ is visible as fringe contrast.

4.7 Discussion

Rhombus loops formed by electron irradiation in 'slow grown' specimens of copper aluminium alloys were found to be interstitial in nature, of Burgers vectors $b = \frac{a}{2}\langle 110\rangle$ and lying on planes near {320}. When these loops were imaged under 'weak beam' conditions, the perfect dislocation was found to be dissociated on the {111} planes into Shockley partials. It seems likely that such dissociation stabilizes these loops in the rhombus configuration and prevents rotation around the <100> axis. Evidence of this can be observed when the shape of rhombus loops grown in Cu .077% Al and Cu .15% Al alloys is compared to those grown in Cu 16% Al. The loops in the dilute alloys have sides with greater curvature than those in higher alloys which suggests that loop rotation can occur to a greater degree in the low alloys (i.e. when the width of partial dissociation is smaller).

A model has been proposed, for the formation of rhombus loops in copper aluminium alloys, by which a Frank loop transforms by shear to a perfect loop free to rotate to a {320} normal. However, this mechanism was not observed in the experiments performed for this thesis and thus it is possible that the transformation occurred when the loop size was small, or that loops nucleated directly on the {110} planes. Further experiments

to link loop size with rotation proved inconclusive as a result of foil stresses, the restriction on the motion of Shockley partials and by the presence of the foil surfaces. Each Burgers vector was found to be associated with two loop planes, on either side of the {110} plane, so that a total of twelve rhombus loops are possible, though it is not easy to identify the different loop planes in conventional strong beam micrographs.

The main aim of the experiment has however been performed; that of resolving the dissociation of the perfect dislocation into Shockley partials.

CHAPTER 5

The Nature of Elongated Defects Formed in Electron Irradiated Copper Aluminium Alloys

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5.1 Introduction.

The presence of linear defects in p type (boron doped) silicon foils implanted with P^+ or Si^+ ions has been reported by Madden (1971) and Seshan (1975). Madden and Wu (1974), on the basis of extensive contrast experiments reported that the linear defects were interstitial, faulted and best described by a Burgers vector of the type $\frac{1}{k}$ [001]. Similar shaped defects have been observed in foils of copper aluminium alloys which were electropolished at temperatures > -55^{o}C and irradiated in the H.V.E.M. The present experiments, were undertaken, to characterize the nature of the loops and obtain evidence as to the defect growth.

Fig. 5/1 demonstrates the differences in loop density and nature that occurs after irradiation of Cu 16% Al specimens polished at (a) -30^{o}C, (b) -75^{o}C. Foils electropolished at high temperatures nucleated and grew a high density of small perfect loops, along with large elongated loops, while those specimens electropolished at very low temperatures (but irradiated under the same conditions as in fig. (a)) nucleated and grew a low density of rapidly growing rhombus loops.

5.2 Identification of the Loop Side Directions

Figs. 5/2, 5/3 and 5/4 show elongated loops in a foil of Cu 16% Al, which was electropolished at -40^{o}C, 4.4 volts. The orientation of the loop sides were obtained by plotting the projected directions of these sides with the aid of a stereogram, using beam directions of [121], [111] and [211] and diffraction vectors <111>, <200>, <220>, <113>. (The beam directions were calculated with the aid of Kikuchi patterns to within $\frac{1}{2}^{o}$.) For a particular loop imaged at a beam direction of [211] for example, the angle between the loop side direction and a known direction in the foil were plotted on a great circle at 90^{o} to the [211] normal. Since the exact line direction must lie on the line joining the beam normal and the projected line direction, it is possible by superimposing several projected directions on the same stereogram to find

out exactly the loop side directions. In the case of these elongated loops, only the long side can be identified and this only was measured.

Fig. 5/5 illustrates on a stereogram the directions of loops imaged in figs. 5/2-5/4. The directions shown as Uδ or Uβ for example, tend to lie near <121> though deviations of up to 10^{o} on either side of <211> have been observed. Loop sides were rarely observed parallel to <211>, the most common directions being <123> and <235>. These directions were also frequently observed during the growth of Frank loops referred to in chapter 3.

The loops imaged in micrographs 5/2, 5/3 and 5/4 indicate that these defects have the following properties:-

(1) Loops imaged in ±g vectors show inside or outside contrast.

(2) Loops aligned in the same directions in the foil can exhibit strong narrow or weak broad contrast for the same diffracting vector.

(3) Elongated loops were 15 → 20 times larger than the size of the background loops in the same area.

(4) Tilting of the foil did not increase to any significant extent the width of the loops.

(5) A large proportion of the loops have irregular contrast, indicating that they lie on inclined planes.

(6) Some of the loops appeared in residual contrast when imaged in <111> reflections.

Loop α for example, was out of contrast when g = $[1\bar{1}\bar{1}]$ fig. 5/2, which suggests that its Burgers vector may be $\pm \frac{a}{2}[0\bar{1}1]$. Since the defect line direction is along $[\bar{2}11]$, the loop is pure edge. Similarly, loop δ along [112] was out of contrast when g = $[11\bar{3}]$ giving a Burgers vector $b = \pm \frac{a}{2}[1\bar{1}0]$.

5.3 Burgers Vector Analysis

Figs 5/6 and 5/7 illustrate the contrast from elongated loops imaged in several different diffraction vectors. Quite clearly, tilts of 35^{o}

produce no change in loop width, thus making an exact analysis of loop habit plane difficult. After the loops were imaged in all three <111> reflections, it was possible to assign unambiguously Burgers vectors of the type $b = \pm \frac{a}{2} \langle 011 \rangle$ to all the loops. Micrographs 5/6 and 5/7 suggest that there exist twelve different loop orientations, of which three loops A, B and R lie on the (111) plane. Loops growing on this plane tend to show uniform contrast along their length and are generally very much larger than those on the inclined planes. Elongated loops growing parallel to the foil surface can in some specimens, reach sizes of 4000 - 5000 Å, while those on the inclined planes were restricted by foil thickness to about 2000 Å in length. Table 7 shows the analysis of the loops in figs 5/6 and 5/7 and it can be seen that for each Burgers vector, there are two rod line directions of $b = \frac{a}{2}[1\bar{1}0]$ then the rod can lie on the (111) plane along $[\bar{1}\bar{1}2]$ or on the $(\bar{1}\bar{1}1)$ plane along [112]. This relationship between Burgers vector $\bar{b}$ and defect line direction $\bar{U}$ is shown in the stereogram fig. 5/8 for loops on the $\alpha(\bar{1}1\bar{1})$, $\beta(1\bar{1}\bar{1})$, $\gamma(\bar{1}\bar{1}1)$ and $\delta(111)$ planes. Thus if $b = \frac{a}{2}[1\bar{1}0]$, two loops $b\delta 3$ and $b\gamma 1$ are expected, with line directions along $[\bar{1}\bar{1}2]$ and [112] as shown. Fig. 5/9 illustrates the nature of the loops that have been considered but only (c) satisfied the observed contrast.

The nature of the habit planes of these loops is difficult to ascertain because only one side could be observed. However, if one of the sides lies along $[2\bar{1}\bar{1}]$ for example, the loop plane must lie near $(0\bar{1}1)$, $(1\bar{1}3)$, (102), (213) or (111), fig. 5/10 line (A). If, as is more likely, the line direction lies near $[\bar{3}21]$, then curve B shows the possible habit planes. The habit planes of the loops are unlikely to be {111} for the following reasons:-

(1) The Burgers vector would be in the same plane as the loop, which would allow glide to very irregular shapes.

(2) Loops formed on the {111}planes would have nucleated as Frank

Table 7

Loop Analysis Based on Contrast from

figs. 5/6 and 5/7

			$g_1.b$	$g_2.b$	$g_3.b$	$g_4.b$	$g_5.b$	$g_6.b$
Loop	$\bar{b}$	$\bar{U}$	$11\bar{1}$	$1\bar{1}\bar{1}$	$\bar{1}1\bar{1}$	$\bar{2}00$	$20\bar{2}$	$3\bar{1}\bar{1}$
S,N	$\pm\ \bar{1}01$	121	-1	-1	0	+1	-2	-2
R	$\pm\ \bar{1}01$	$\bar{1}2\bar{1}$	-1	-1	0	+1	-2	-2
L	$\pm\ 011$	$\bar{2}\bar{1}1$	0	+1	0	0	-1	-1
J	$\pm\ 011$	$\bar{2}1\bar{1}$	0	+1	0	0	-1	-1
X	$\pm\ 110$	$1\bar{1}\bar{2}$	+1	0	0	-1	+1	+1
W	$\pm\ 110$	$\bar{1}1\bar{2}$	+1	0	0	-1	+1	+1
I	$\pm\ 0\bar{1}1$	211	-1	0	-1	0	-1	0
B	$\pm\ 0\bar{1}1$	$2\bar{1}\bar{1}$	-1	0	-1	0	-1	0
H	$\pm\ 101$	$\bar{1}\bar{2}1$	0	0	+1	-1	0	+1
F	$\pm\ 101$	$1\bar{2}\bar{1}$	0	0	+1	-1	0	+1
U	$\pm\ 1\bar{1}0$	112	0	+1	-1	+1	+1	+2
A	$\pm\ 1\bar{1}0$	$\bar{1}\bar{1}2$	0	+1	-1	+1	+1	+2

loops, which subsequently sheared to perfect nature. It is not however possible to form loops of $b = \frac{1}{2}[\bar{1}01]$, $\frac{1}{2}[01\bar{1}]$, or $\frac{1}{2}[1\bar{1}0]$ by shear of Frank loops on the (111) plane.

(3) Loop directions other than <211>, <532> or <123> would be observed, since the shape of sheared Frank loops on {111} planes indicate that curved dislocation segments soon develop, chapter 3.

The other alternative and more likely possibility, is that the loops nucleate directly on {011} planes and rotate subsequently to planes nearby, in a similar manner to the rhombus loops discussed in chapter 4. Thus for loops aligned along <211> directions, the habit planes would be exactly {110}, while for loops along <532> or <321> the habit planes would rotate to near {012}. It is inherent in this argument that the loops nucleate directly on {110} planes rather than on {111} planes as Franks followed by a transformation to perfect nature, since close observation of the linear defects under growth suggests that they initially form along <112> directions. Thus, all the features of the observed contrast can be explained if these defects are assumed to be characterized by $\bar{b} = \frac{a}{2}$ <110>, $\bar{U}$ = <112> and lying somewhere near {011} planes. The possible configurations are shown in table 8.

Stereopairs of linear defects, imaged in $g = [\bar{2}20]$, $z = [111]$ revealed that the loops aligned along $[\bar{1}\bar{1}2]$, $[\bar{1}2\bar{1}]$ and $[2\bar{1}\bar{1}]$ directions grew parallel to the foil surface and at all depths in the foil (except for a denuded zone of about 400 Å which was common to both rods and background loops). There also appeared to be an asymmetry in the distribution of loops on the various planes, with most of the loops being parallel to the foil surface. While the stereos revealed that elongated loops do not grow near foil surfaces, little information was gained as to the habit planes.

There are many interesting details of contrast in figs 5/6 and 5/7.

(1) Loop A fig. 5/7(f) appears to be rotating its habit plane from

Table 8

Elongated Loops which Should be Observable

Plane	Line Direction		$\bar{b}$	$\bar{n}$
α $(\bar{1}1\bar{1})$	Dα	121	$\bar{1}01$	$\bar{1}01$
	Cα	$\bar{2}\bar{1}1$	011	011
	Bα	$1\bar{1}\bar{2}$	110	110
β $(1\bar{1}\bar{1})$	Dβ	211	$0\bar{1}1$	$0\bar{1}1$
	Aβ	$\bar{1}1\bar{2}$	110	110
	Cβ	$\bar{1}\bar{2}1$	101	101
γ $(\bar{1}11)$	Dγ	112	$1\bar{1}0$	$1\bar{1}0$
	Bγ	$1\bar{2}\bar{1}$	101	101
	Aγ	$\bar{2}1\bar{1}$	011	011
δ (111)	Aδ	$\bar{1}2\bar{1}$	$\bar{1}01$	$\bar{1}01$
	Bδ	$2\bar{1}\bar{1}$	$0\bar{1}1$	$0\bar{1}1$
	Cδ	$\bar{1}\bar{1}2$	$1\bar{1}0$	$1\bar{1}0$

For each burgers vector, there are two line directions e.g. b = $\bar{1}01$ u = $\bar{1}2\bar{1}$ and 121

one end of the loop to the other. This can also be observed on another loop at point α.

(2) Defect G is not in contrast in any diffraction vector. While it is not likely that this defect is a loop, it could be precipitation along the $[2\bar{1}\bar{1}]$ direction. It is of interest to note that a number of the linear defects grow initially with this form of contrast at the centre and two regions of good contrast at both ends. An example can be observed in fig. 5/11(c). The loop should be in good contrast, since $b = \frac{a}{2}[10\bar{1}]$. Fig. 5/11(A), a weak beam micrograph imaged in g $[02\bar{2}]$, shows structure inside the loop, which may be associated with precipitation. Similarly loop δ fig. 5/6(a) imaged in g $[11\bar{1}]$ exhibits residual contrast at the loop centre which shows a fine structure split into two lines. The ends of the loop appear in good contrast.

(3) Loop ψ fig. 5/7(f) also shows an interesting contrast effect. The double arc contrast of the small loop appears to extend two lines outwards and parallel to the line of no contrast in the centre of the loop. These two dislocation lines were always imaged in very weak contrast, similar to that of defect G. No conclusions were obtained as to the reasons for these types of contrast.

5.4 Weak Beam Images of Elongated Loops

It is possible for these linear defects to reduce their energy by dissociating into Shockley partials in a reaction of the type:-

$$\frac{1}{2}[\bar{1}01] = \frac{1}{6}[\bar{1}\bar{1}2] + \frac{1}{6}[\bar{2}11]$$

with the component partials gliding on the (111) plane. Weak beam micrographs were taken (using the JEM100C microscope) of linear defects in a Cu 16% Al foil, which had previously been electron irradiated in the H.V.E.M. Twelve distinct types of loops were observed when imaged in <111> and <220> diffraction vectors at the <111>, <211> and <110> beam normals.

Figs. 5/12, 5/13 and 5/14 show elongated loops when imaged under such conditions. It was only possible to resolve the dissociation of those loops whose directions were parallel to the foil surface, since the nine loops on the inclined {111} planes were at such an angle that detail could not be resolved. The dissociations observed were:-

$$\text{Loop A} \quad b = \frac{1}{2}[0\bar{1}1] \rightarrow \frac{1}{6}[\bar{1}\bar{1}2] + \frac{1}{6}[1\bar{2}1]$$

$$\text{Loop B} \quad b = \frac{1}{2}[10\bar{1}] \rightarrow \frac{1}{6}[2\bar{1}\bar{1}] + \frac{1}{6}[11\bar{2}]$$

$$\text{Loop D} \quad b = \frac{1}{2}[1\bar{1}0] \rightarrow \frac{1}{6}[2\bar{1}\bar{1}] + \frac{1}{6}[1\bar{2}1].$$

When $g = [0\bar{2}2]$ both partials $\frac{a}{6}[\bar{1}\bar{1}2]$ and $\frac{a}{6}[1\bar{2}1]$ are calculated to be visible and these can be observed in loop A fig. 5/12(a). Both partials can be imaged in loop B fig. 5/12(d) in $g = [\bar{2}02]$ and loop D fig. 5/12(c), $g = [\bar{2}20]$. The loop Burgers vector analysis was performed by imaging the defects in <111> diffraction vectors as shown in fig. 5/13.

The proper sequential arrangement of partial dislocations to form an enclosed intrinsic stacking fault is that on viewing the perfect dislocation $\bar{C}\bar{B}$ from outside the tetrahedron and along the positive sense of the line the Greek-Roman partial is on the left, with the Roman-Greek partial on the viewers right, fig. 5/15(a). In fig. (B) the role of the partials has now been reversed, which would cause an A-A stacking arrangement. This can be avoided if it is envisaged that each partial in turn is dissociated into two other partials:-

$$\bar{C}\bar{\delta} \rightarrow \bar{\delta}\bar{A} + \bar{\delta}\bar{B}$$

$$\bar{\delta}\bar{B} \rightarrow \bar{A}\bar{\delta} \quad \bar{C}\bar{\delta}$$

The resulting partials may then rearrange themselves to form an extrinsic fault. The final displacements produced by the two dissociations are identical but the energies involved in the two modes may be different.

Weak beam microscopy has revealed that loops having the same Burgers vector and line direction, exhibit different contrast in any

g <220> diffraction vector. In fig. 5/12(b) for example, loops B and L have $\bar{b} = \frac{a}{2}[10\bar{1}]$ and $\bar{U} \triangleq [1\bar{2}1]$, though the former has broad contrast, while the latter has its partials overlapping, to exhibit narrow contrast. Excluding the possibility that vacancy loops are present the configurations of elongated loop that may form are shown in fig. 5/16. If the positive sense of the dislocation is defined as pointing into the paper, an intrinsic stacking fault is formed, if with the uppermost dislocation, the partial $\bar{\delta}\bar{B}$ is on the left and an extrinsic fault if $\bar{\delta}\bar{B}$ is on the right. For each Burgers vector and line direction, two possible loop orientations are allowed, each rotated a few degrees on either side of the {110} plane. In total, four possible configurations are allowed, of which two, the extrinsic fault configurations were not considered because $\gamma_E \geq \gamma_I$ Gallagher (1966).

When $g = [0\bar{2}2]$, δC was the outer partial in loop B but inner partial of loop L. In fig. 5/14(K) the configuration reversed when $\bar{B}\bar{\delta}$ alone was in contrast. Loop B showed it as the inner partial, while in loop L it appeared as the outer partial. The observed contrast can only be explained by the assumption that the loop normals of Loops B and L lie on opposite sides of the $(10\bar{1})$ plane. Loop B is represented by diagram fig. 5/16(c) with $\bar{\delta}\bar{C}$ as the outer partial. Fig. (A) describes the geometry of loops L, with $\bar{B}\bar{\delta}$ as the outer partial. When loops B and L were imaged in $\pm g = [20\bar{2}]$, fig. 5/12(B) and (D) the contrast changed from broad to narrow and vice versa.

Fig. 5/17 illustrates the explanation of strong narrow images and weak wide images formed by elongated loops. If a non-edge loop of small height is considered, there are two local regions A and B where the lattice planes are bent in opposite senses. B regions have anticlockwise rotations, while A regions have clockwise rotations. The loop image width depends on which of the two regions A or B gives rise to the diffraction contrast. As the two B regions are close together, the

rotations have greater magnitude. So if the diffraction conditions are such that the B regions are responsible for contrast, the loop will appear strong and narrow on the micrograph, while the A regions produce wider images of weak contrast.

Taking into account the fact that loop planes can be inclined in opposite directions, 24 possible configurations of elongated loop can occur, of which 15 have been observed. Fig. 5/18 is a representative schematic diagram for the loops B and L with line directions parallel to the foil surface. If the line direction of loop B is defined as shown in the upper diagram, the partials $\bar{\delta}\bar{C}$ will be imaged on the outside, implying that the loop plane slopes downwards from left to right. Loop L will thus be inclined in the opposite sense, to give the observed contrast.

It is interesting to observe that loops exhibiting broad contrast tended to lie in a different direction, to those showing narrow contrast. This phenomena is illustrated in fig. 5/19, in three elongated loops with the same Burgers vector $b = \frac{a}{2}[10\bar{1}]$. Loop ψ in this reflection has narrow contrast and lies with its long direction 6^{o} from $[\bar{1}2\bar{1}]$, towards $[10\bar{1}]$. Loop ξ on the other hand is imaged in broad contrast and has a line direction $\triangleq 2^{o}$ from $[\bar{1}2\bar{1}]$ towards $[\bar{1}01]$. Loop ϕ is a very interesting example of a linear defect showing both forms of contrast. The line direction of ϕ is almost parallel to $[\bar{1}2\bar{1}]$ and it was concluded from this observation that defects lying on opposite sides of the <112> direction lie on planes a few degrees on either side of {110}. Fig. 5/20 depicts the partial configuration, which can be explained by allowing the loop normal to change from one side of [110] to the other. In doing so, the Shockley partials change from one side of the loop to the other, to preserve the enclosed intrinsic stacking fault.

5.5 The Effect of Specimen Electropolish Conditions on the Formation of Elongated Loops

Matthews and Ashby (1973) have investigated the type of damage

formed in silicon specimens as a result of electron irradiation in a H.V.E.M. operating at 1 MeV. By using a hot stage specimen holder they observed the damage formation as a function of both time and temperature. When the specimen temperature was 450°C or greater, they observed the presence of linear defects parallel to the <110> direction. It was suggested that these rods were probably precipitates of an impurity such as copper, carbon, or oxygen rather than phosphorus or boron, since they were imaged in both n and p type material. Madden (1973) concluded that H.V.E.M. damage in silicon at 500°C consists of planar defects involving the {311} planes, which is in agreement with results of Booker and Joyce (1966), which indicate that the low energy planes of silicon were of the type {311}.

The linear defects in electron irradiated copper aluminium form under different conditions compared to those in silicon. Irradiation experiments in the H.V.E.M. at elevated temperatures on freshly prepared foils, revealed that specimen electropolish conditions influence the extent to which elongated loops nucleate and grow. Fig. 5/21 summarizes the types and densities of loops formed as a function of polishing voltage and temperature in foils of Cu 16% Al irradiated in the microscope under identical conditions. Three regions were observed:-

(A) Specimens polished at low temperatures and high voltages nucleated a low density of rhombus loops.

(B) The shaded region indicates the area where medium densities of rhombus loops formed.

(C) Specimens polished at high temperatures and low voltages produced a high density of rhombus loops surrounding a high density of linear shaped loops.

The dramatic differences in loop density have already been illustrated in fig. 5/1.

Specimens polished over such a wide range of temperatures and

voltages nucleated on irradiation, a broad spectrum of loop densities for similar irradiation conditions, thus making a quantitative analysis of radiation damage measurements impossible.

The cause of this variation was not traced to specimen preparation until many other irradiation variables had been investigated. Experiments were devised to investigate the effects of microscope vacuum, foil thickness, surface contamination, specimen temperature and dose rate. The temperature and voltage of the electropolish bath were then varied in an attempt to produce the 'ideal' specimen. Various power supplies were used with different 'ripple factors', but no observable differences resulted. Good specimens were produced quickly at temperatures of $\triangleq -40^{o}C$ and 4.4 volts. The experiments were then extended to include very low temperatures of $-75^{o}C \rightarrow -80^{o}C$ and to decrease the polishing time, the voltage was increased to $\triangleq 6.5$ volts. These conditions had not been used previously in the production of specimens because of the long polishing times required, ($1-1\frac{1}{2}$ hours for the final foil thinning). However, the specimens made under such condition were clean and had large thin areas suitable for electron microscopy. Electron irradiation of such specimens produced no linear defects. Furthermore, consistent results from different specimens were obtained. The investigation was then extended over the widest range of polishing conditions, (consistent with good specimens being obtained). Each specimen was then irradiated as soon as it had been removed from the polish bath. Fig. 5/21 indicates that for reproducible results, low temperatures and high polishing voltages must be used.

The conditions within an electropolish bath are complex. Hydrogen is produced at the cathode and may charge the solution with gas and be evolved from the electrode as bubbles. Hydrogen from the solution may be absorbed on the anode in a concentration corresponding to its effective chemical potential in combination with its mobility in the metal

and there ionized Erdey-Gruz (1972), to assist in charge transfer through the bath. Since oxygen cannot diffuse into the specimens at those temperatures, hydrogen is the only species present or produced at the anode that can diffuse sufficiently rapidly to penetrate the specimen at or below room temperature. White (1973) concluded that the presence of hydrogen helped improve the contrast of γ' particles in PE16 and more recently, Buswell (1974) has suggested that hydrogen introduced during the preparation of specimens resulted in an increase of both the number density of voids and the volume swelling of PE16 and Inconel 625, after irradiation in the H.V.E.M.

The amount of hydrogen that can be absorbed by the foil during thinning depends on the difference between the copper or copper aluminium removal rate and the drift velocity of hydrogen into the foil. A crude estimate can be made of the change in drift velocity on the basis of the jump diffusion model for hydrogen in metals. The statistical mechanical treatment of the problem by McLellan and Hawkins (1975) has shown that this model properly describes the motion of hydrogen in the lattice at the temperatures of interest. According to the model the diffusion constant D is a function of the mean jump distance <l> and the mean time between jumps t:-

$$D = D_o \exp\left(-\frac{QD}{RT}\right) = \frac{\langle l^2 \rangle}{6t}$$

For octahedral interstitial sites in the F.C.C. lattice, the ones most likely to be occupied by hydrogen in solution, l is equal to $a/\sqrt{2}$. For hydrogen atom drift along <001> in the crystal, four of the twelve jumps will move the proton into the crystal from the surface by a distance $a/2$. The drift velocity is thus $a/6t$.

Measurements of the polishing removal rates of copper and copper 5% aluminium as a function of polishing temperature at a voltage of 4.4 volts are plotted on fig. 5/22(a). In general for a given technique and

solution, lowering the polishing temperature decreased the polishing rate. The drift velocity of hydrogen in Cu 4 wt% Al, Cu and Cu 8 wt% Al has been plotted as curves (a), (b) and (c), from data of hydrogen diffusion in copper aluminium alloys Mokaram (1974). It is doubtful whether activation energies for diffusion at 600°C could be extrapolated to -75°C accurately, but accepting this limitation the results are useful as an order of magnitude calculation.

One problem experienced in the accurate determination of electropolishing rates was that small temperature rises in the jetting solution altered appreciably the jet polish rates, with the consequence that the final electropolish rates were not reproducible. However, when corrections to the jet polishing rates were made, to reflect the changes in jet polish temperature and final electropolishing rates calculated by taking the average for many specimens, accurate removal rates could be established at each temperature.

Table 9

Table Showing the Incidence of Elongated Loops Under Given Irradiation Conditions for a Selection of Copper Aluminium Alloys

Cu 16% Al	el. loops		
Cu 10% Al	el. loops		
Cu 5% Al	el loops		
Cu 2% Al		high ρ	
Cu.98 Al		high ρ	
Cu.31 Al		high ρ	
Cu.15 Al			Low ρ
Cu.08 Al			Low ρ
Cu			Low ρ

ρ = background loop density (rhombus); Specimens polished at -35°C 4.4V; Irradiation temp. ≃ 240°C; Dose rate 6 x 10^{18} el./cm^2/sec; Thickness ≃ 2200 Å; Max. time between polish and irradiation = 300 seconds.

thus within the accuracy of the drift velocity calculations and specimen removal rates, hydrogen can enter the surface of the crystal during thinning at -35°C, but little should enter during thinning at -75°C. It was not possible to determine the average concentration of hydrogen in the specimens due to the volume of the specimen and the small quantity of hydrogen involved. Attempts were made, to correlate the density of elongated loops with polishing rate, by polishing specimens of Cu 16% Al at different rates, but no pattern was detected however, due to the fact that the constant removal of copper aluminium atoms from the surface during thinning did not allow equilibrium conditions to be maintained.

5.6 Effect of Alloy Concentration on the Nucleation of Elongated Loops

The nucleation and growth of elongated loops appeared to be critically dependent on the density of background clusters, irradiation temperature and alloy concentration. Table 9 shows the incidence of elongated loops as a function of alloy concentration, after irradiation under similar conditions. Elongated loops have only been observed in alloys of concentration >2 at% Al. In the intermediate alloy range Cu .31% Al, Cu .98% Al and Cu 2% Al a medium to high density of background rhombus loops were created during irradiation, while in the dilute alloys Cu .08% Al and Cu .15% Al a low to medium density of dislocation loops was observed. Pure copper appeared to be the only metal examined, in which no observable increase in loop density was noted. This effect is demonstrated in fig. 5/23 and shows the loop configurations when three alloys, Cu .15% Al, Cu 2% Al and Cu 16% Al were electropolished at -35°C, 4.4 volts and irradiated in the H.V.E.M. at T_i = 240°C immediately after the polish treatment. The Cu .15% Al specimen fig. (A) has a much higher loop density than it would have if electropolishing had been performed at -75°C. The Cu 2% Al specimen has nucleated a very high density of loops but no rod defects, while the Cu 16% Al exhibits a high density of rhombus loops along with many rod loops. It is concluded

from these observations and the hydrogen drift velocity calculations, that hydrogen can diffuse into all the metals while they are being polished at temperatures $>-60^{o}C$. Copper aluminium alloys polished at $-60^{o}C$ and 6.5 volts appeared to show little evidence of hydrogen penetration. Pure copper also showed little evidence of gas pickup, even in specimens polished at room temperature, though Kenik and Mitchell (1975) observed a lowering of the threshold energy when hydrogen gassed copper specimens were irradiated in the H.V.E.M. at room temperature.

To account for this observation, it is postulated that the hydrogen is not being trapped in the lattice but is allowed to diffuse out of copper specimens when they are heated above room temperature. For the alloys, the hydrogen gas appears to be trapped by impurities and only diffuses out when the specimens are annealed at temperatures between $260^{o}C$ and $300^{o}C$. The degree of hydrogen retention in the crystal depends on the amount of impurity present and it is significant that a maximum in background density of rhombus loops occurs at Cu 2% Al which, according to Mokaram (1974) offers the highest solubility to hydrogen of any of the copper aluminium alloys. It appears possible that in the high alloy concentrations, vacancy-aluminium hydrogen gas complexes can be established which because of the density of aluminium atoms in the lattice can form and join up into rows along $\triangleq$ <211> directions. Why this direction is preferred over the more common <110> direction is unclear, though it is interesting to note that anisotropic calculations by Brown (1967) suggest that dislocations whose line directions are parallel to <211> have their lowest energy. When the aluminium concentration is not high enough to promote the formation of elongated loops then the hydrogen atoms trapped in the lattice may be knocked on by the incident electrons to cause displacement of the lattice atoms, giving rise to a locally higher number of di-interstitial nuclei and loop density.

5.7 Elongated Loop Densities

One of the most significant results obtained in the present set of experiments, was the relationship between the elongated loop density and background loop density. Fig. 5/22(b) illustrates this effect with a graph of elongated loop density plotted against corrected background loop density for a foil of Cu 16% Al. Since there existed a considerable asymmetry in the distribution of elongated loops on the {111} planes, only loops with their long sides on the (111) plane were counted. Further, it was also very difficult to recognize loops lying on the steeply inclined planes. The background densities were adjusted by varying the dose rate, irradiation temperature or annealing temperature.

If the hydrogen had no time to diffuse out of the specimens, loop densities $>3 \times 10^{16}/cm^3$ were measured, after irradiation at $T_i = 240^{\circ}C$. When these very high densities occur no elongated loops were observed, indicating that rods and rhombus loops are nucleated at the same time. It is likely that the presence of rhombus loops of differing Burgers vectors prevents the rapid growth of the rods. As the background loop density was reduced to about $2.8 \times 10^{16}\ cm^{-3}$, a high density of rods was observed. Reduction of the background density still further reduced the rod density until at a background density of $\triangleq 6 \times 10^{15}\ cm^{-3}$, no elongated loops grew. It is assumed that the rods need a large amount of volume in which to grow, since their line direction is uniquely <112>. Any nucleation of defect clusters in the path of a growing rod prevents its extension. At the same time, results indicate that the rod length alters as the background loop density changes. In thin areas of specimen, rod defects can grow to a very large size, but as the background density increased, the rod length decreased. However these results are only qualitative, as there appeared to be a very wide spread in the rod size.

Fig. 5/24 illustrates the effect of specimen thickness on elongated loop size and density. In (a), a thin area of a Cu 16% Al foil, the

measured density was low, with the consequence that rod defects can grow rapidly, as there was no obstruction to growth. A thick area of foil tended to prohibit the growth of rods, in accordance with fig. (b).

A similar effect was noted when a Cu 16% Al specimen was irradiated at different dose rates. Fig. 5/25(b) shows an area of Cu 16% Al foil irradiated at a generation rate of 3.8×10^{19} cm^{-3} sec^{-1}, to produce a high incidence of rhombus loops, but no elongated loops. Subsequent irradiation at a dose rate of 7×10^{18} $cm.^{-3}sec.^{-1}$ fig. (a) nucleated a lower density of rhombus loops but a very high density of elongated loops. The time interval between the two micrographs was short, allowing no time for the hydrogen to diffuse out of the foil. Since the thickness and irradiation temperature of the two areas were similar, the experiment indicated that the size and density of elongated loops is critically dependent on the total loop density. In fig. (b), so many loop nuclei of different Burgers vectors are formed, that it is impossible to extend a rod in any <112> direction without impinging on one of these loops. Loops of similar Burgers vectors would allow amalgamation and this was sometimes observed, but the probability is that at high densities, loops of dissimilar Burgers vectors were being encountered.

5.8 Effects of Irradiation Temperature

Most of the experiments to determine the characteristics of rod loops, were carried out at a temperature of $\simeq 240^{\circ}C$. Quite fortuitously, this irradiation temperature caused the formation of the largest size of rod defect. The relationship between irradiation temperature and loop size was determined by irradiating a specimen initially at low temperatures and then increasing the temperature for a further irradiation on a new area. This method prevented the release of hydrogen gas from the specimen, which would have occurred, if high temperatures had been used initially. The results are illustrated in fig. 5/26. (A) shows a plot of loop size against irradiation temperature on a single specimen, whose

temperature was increased in a stepwise manner. Graph (B) shows the loop size at high temperatures measured from several specimens irradiated immediately after insertion into the microscope. The differences between graphs (A) and (B) are probably due to the annealing that has taken place in specimen (A).

The graphs indicate, that at temperatures <135°C no elongated loops form. As the irradiation temperature was increased, the size of defect increased, suggesting the rods are formed when hydrogen gas can diffuse short distances in the foil. A maximum rod size was obtained at about 240°C above which the rod size reduced rapidly. Measurements indicate that at irradiation temperatures of 135°C the rod size was not much larger than the background loop density, while at 240°C the rod size at the moment when longitudinal growth ceased was four or five times larger than the background density. Thus, the rod size is not only dependent on the interstitial velocity but on the mobility of hydrogen in the lattice.

5.9 Mechanisms of Elongated Loop Growth

The main distinguishing feature of these loops is their rapid speed of growth. Specimens of Cu 16% Al doped with hydrogen tend to reach sizes of 2000 - 3000 Å in a few seconds, depending on the irradiation conditions. In order to observe the early stages of growth, irradiation temperatures of about 210°C were used, together with a dose rate of about 10^{18} el./cm^2/sec. The main problem experienced in the recording of loop growth was to establish good two beam conditions at the beginning of the irradiation. The usual procedure was to irradiate one area as a marker, establish the diffraction conditions then move to an adjacent area in order to record the loop growth.

A common feature in the growth of these loops was the instantaneous appearance of a line of weak contrast along the <112> directions. As the irradiation time was increased, the loop contrast gradually changed, to become stronger and exhibit the features associated with an elongated

dipole loop. Fig. 5/27 demonstrates the differences in growth rates between an elongated loop and the small background loops shown in 5/28. Elongated loops grow rapidly for the first minute of irradiation, reduce their velocity and then stop growing. In the plateau region, the rod defects are still absorbing interstitials but increase in width only. The rate of growth of the background clusters is extremely low, in these micrographs, .62 Å/sec for rhombus loops growing under identical conditions in undoped copper aluminium specimens.

Quite clearly, the interstitial velocity in hydrogen doped foils has been reduced substantially by the presence of hydrogen. (The high loop density is evidence of this). It seems probable that elongated loops in the initial stages are growing by a precipitation process activated by the electron beam. (Unirradiated foils showed no evidence of any weak contrast line defects). Another common feature of rod growth is the change in defect line direction along its length. This contrast is visible in fig. 5/28, as a change in loop side direction of about 8^{o}. Fig. (D) also shows clearly the increase in loop width, but not length, after an irradiation period of 5 minutes. Another important feature in the growth, is that loops with sides on the (111) plane soon broaden and intersect the foil surfaces though in many cases, the loop width was prevented from increasing, by the pinning of the partials by small loops present in the foil.

Fig. 5/29 indicates possible mechanisms of elongated loop growth. In the initial stages of irradiation, a rod like defect appears with weak contrast, which remains the same, when imaged in all reflections. It may be possible that a line of dilation is formed, fig. (a), due to the agglomeration of vacancy, aluminium hydrogen complexes into a line. However, the properties of dilation lines can be identified by three main factors:-

(1) The centre of inversion of symmetry of their images.

(2) The unrelated nature of images in ± g.

(3) The invisibility of the image with a reflecting vector along the line of the defect. Humble (1969).

Since the early stages of the defects are out of contrast, it seems unlikely that the contrast can be explained in this manner. It is also difficult to explain the transition from a dilation line to an elongated dipole loop. Another possible explanation, is that the defects form with two very closely spaced glide dislocations of opposite sign having a very weak contrast. In fact according to Humble, closely spaced dipole dislocations can have images with similar symmetry properties and character to those of a dilation line. Blank and Amelinckx (1963) have investigated tracks in uranium dioxide crystals and have attributed some of the contrast effects in thin foils to the presence of dilation lines. The contrast from the tracks was extremely weak and the symmetry properties not apparent from the micrographs. Thus, with the evidence available at present, it is not possible to distinguish between the two possibilities.

On many occasions, small rod loops were observed to amalgamate and form large loops. Such an example can be seen in fig. 5/30, in which three distinct rods fig. (A) grew into one long loop. The change in loop contrast can be observed when figs (a) and (b) are compared. The rapid growth of rods may be explained as an aglomeration of small lines of dilation or narrow spaced dipoles in the early stages of irradiation.

Fig. 5/31 shows another growth sequence of loops irradiated at 240°C. Loop A on an inclined {111} plane appears to form as an amalgamation of smaller rods, while C appears at 120 secs. in weak contrast, but changes to normal dipole contrast after 260 secs. Fig. 5/29 (c) is illustrative of the nature of elongated loops, after rapid growth has ceased. The Burgers vector $\bar{B}\bar{A}$ for example can dissociate into Shockley partials $\bar{\delta}\bar{A}$ and $\bar{B}\bar{\delta}$ on the (111) plane. This reaction has been imaged

using weak beam diffraction conditions. The end dislocation segment remains undissociated and may not be confined to any particular plane. It is thus possible for the rod to expand rapidly by the climb of the small end of the loop. As the radiation is increased, the elongated loop may stop growing and commence to broaden or rotate its loop plane. This can occur, because the jog $\overline{BA}$ climbs onto the $(\bar{1}1\bar{1})$ plane where it can dissociate into partials $\overline{\alpha B}$ and $\overline{C\alpha}$. Loop rotation can be accommodated by glide of the partials on this $(\bar{1}1\bar{1})$ plane, in a manner similar to rhombus loop rotation.

An elongated loop which grew large and intersected the foil surface was imaged under weak beam conditions fig. 5/32. Both partials can be clearly seen in the {220} reflections. Also imaged in the micrograph are smaller rhombus loops showing a similar contrast. It can thus be seen that when elongated loops are large, they resemble rhombus loops. The loop sides on the steeply inclined planes of the large loop have probably been attracted to the specimen surface by contamination stresses. The constrictions along the partials suggest the presence of stair-rods at the growing ledge on the loop sides, though no evidence has been accumulated to verify this. Referring back to 5/29, it is likely that stair-rods $\overline{\alpha\delta}$ and $\overline{AB}/\overline{\alpha\delta}$ join the extended dislocations at the junction of the {111} planes so that the ultimate shape of the rod loop is an elongated rhombus loop.

The rod loop increase in size by the passage of superjogs or constrictions along the stacking fault and this can be observed in fig. 5/33 loop α, where the large elongated loop in contrast shows many such constrictions along the loop side.

5.10 Effect of In-Situ Specimen Annealing on the Formation of Elongated Loops

It has been established in this thesis that the maximum density and size of elongated loops occur at irradiation temperatures $\simeq 240^{\circ}C$, when

the background cluster density $\simeq 3 \times 10^{16}$ cm^{-3}. However, it is possible to release the hydrogen from its impurity traps by short anneals at temperatures up to 340°C. When hydrogen doped specimens were annealed for 1 hour at 240°C most of the residual gas was released. At an anneal temperature of 340°C the hydrogen can be released in under five minutes. Fig. 5/34 illustrates the background loop density as a function of anneal time at various temperatures and shows the increased rate of reduction in loop density as the temperature of anneal was increased. Irradiations were performed on different areas of the specimen, but under identical conditions at T_i = 240°C, with the annealing treatments between the irradiations. The presence of elongated loops was also dependent on the time or temperature of anneal and this reduction can be observed in fig. 5/35, which illustrates the damage observed when a foil of Cu 16% Al was electropolished at -15°C 2.2 volts and subjected to the following anneal treatments:-

(a) irradiation at 240°C. No anneal,

(b) irradiation at 240°C after a 10 minute anneal at 240°C,

(c) irradiation at 240°C after 2 minutes anneal at 295°C,

(d) irradiation at 240°C after 2 minutes anneal at 315°C.

After a five minute anneal at 380°C, the loop density observed after irradiation at 240°C appeared to be the same as that for irradiated specimens polished at -75°C without an anneal. By this technique, it was possible to standardise all specimens before attempting to measure the loop density as a function of irradiation temperature. Without this treatment, specimens irradiated under nominally the same conditions tended to give widely varying results.

5.11 Some Observations of Elongated Frank Loops

In addition to the more commonly observed elongated perfect loops, elongated Frank loops were seen in several Cu 16% Al specimens, though the exact mechanism of the growth of these loops is at present unknown.

Loop T fig. 5/36 (a) and (b) shows such a loop, whose plane is (111). When g = $[1\bar{1}1]$ z = [110], the stacking fault between the dissociated Shockley partial and stair-rod dislocation appeared on edge, while after a large tilt to z = [011] fig. (b) the stacking fault on the inclined plane was easily distinguished. Thus the dissociation plane can be identified as $(1\bar{1}\bar{1})$ and the dislocation reaction as:-

$$\frac{a}{3}[111] = \frac{a}{6}[211] + \frac{a}{6}[011]$$

Loop X fig. (c) is another elongated loop, whose line direction is along $[1\bar{1}0]$. This loop appears in contrast when g = $[0\bar{2}2]$ and $[20\bar{2}]$, but out of contrast in g = $[\bar{2}20]$ indicating that the habit plane is $(\bar{1}\bar{1}1)$. Since the rod direction U = $[1\bar{1}0]$, the dissociation plane of the Frank partial dislocation is (111). The Shockley partials $\frac{a}{6}[\bar{1}\bar{1}2]$ are visible when imaged in g = $[20\bar{2}]$ z = [111] fig. (c), but the stacking fault between the dissociated partials is out of contrast.

In fig. 5/37(a) the loops are imaged in the 'edge on' configuration (z = [011]) with only the Shockley partials observable while fig. (b) shows the same area in g = $[0\bar{2}2]$ z = [111]. In fig. 5/37(c) the loops are completely out of contrast, since g = $[\bar{2}20]$. Quite clearly, these loops are of a different nature to the elongated loops discussed earlier in this chapter.

5.12 Conclusion

The presence of elongated dipole loops in electron irradiated metals has been confirmed and attributed to the diffusion of hydrogen into the specimens during the electropolish treatment. Both linear Frank and perfect loops have been observed. The nature of the latter has been established by extensive tilting experiments and weak beam micrographs to be of Burgers vector b = $\frac{a}{2}$ <110>, line direction U $\triangleq$ <112> and loop normal $\triangleq$ <110>. Stereo micrographs also revealed that they lay deep in the foil, implying that the cause was not an impurity diffusing in from

the surface.

Each Burgers vector was observed to be associated with two loops each having their long diameter at right angles to the <110> direction. Each <112> defect line direction was associated with two loop planes of opposite inclination, giving rise to loops imaged in strong and weak contrast for the same diffraction vector. Thus a total of 24 perfect configurations are possible in comparison to the four configurations expected when the loops are faulted.

The most distinguishing feature of these loops was the rapid growth speed in the early stages of irradiation and a mechanism of formation has been explained by assuming that the hydrogen gas can interact with the aluminium impurity atoms present to form very narrow dislocation dipoles along $\triangleq$ <112> directions. A high concentration of aluminium is assumed to be necessary to promote the formation of these loops, since no rod loops were observed in alloys <5% Al. The elongated loop density was also found to be directly dependent on the background rhombus loop density which itself varied as the dose-rate, irradiation temperature and annealing temperature were changed. Weak beam microscopy also revealed that the elongated perfect loops were dissociated with Shockley partials glissile on the {111} planes, while the Frank rod loops dissociated as a Shockley and a stair-rod at the junction of the {111} planes.

Attempts at measuring the activation energy of the loops were frustrated when high temperature in-situ annealing experiments were performed, due to the irregular loop glide which occurred.

Seshan (1975) observed that the majority of loops nucleated in phosphorus implanted silicon were faulted and lay on {111} planes having displacement vectors of the type $\frac{a}{x}$ [111], with x slightly greater than three because of impurity on the stacking fault. Contrast effects in his study indicated that dopant atoms segregate inside the perfect

loop as well as on the stacking faults, which suggests that the perfect loops were originally faulted and that segregation remained after unfaulting. The displacement vectors were of the type $\frac{a}{2}$ <110> - $\frac{a}{y}$ <111>. However, this form of Burgers vector was not observed in electron irradiated hydrogen doped copper aluminium foils, lending support to the argument that the perfect rod loops were not initially faulted. It also seems unlikely that faulted loops would initially form with loop sides along ≙ <112> directions since no dissociation of a Frank loop can occur along this direction. The precipitation of hydrogen along <112> directions may be affected by the presence of short range ordering (known to occur in Cu/Al alloys) or the presence in the foil of other gases which may prevent precipitation along <110> directions.

CHAPTER 6

Experimental Techniques used to Obtain Reproducible Results

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6.1 Introduction

The use of the H.V.E.M. as an electron irradiation facility is an excellent technique for studies of radiation damage and has been particularly applied to the problem of void formation. The main advantage over other methods of irradiation, is that direct observations can be made continuously and the dynamic behaviour of loops, dislocations or voids followed. One can follow the dose dependence of damage relatively quickly in one specimen, avoiding experimental scatter due to the variability of material. High displacement rates can be obtained and an irradiation equivalent to that received by a fuel pin during its lifetime in a fast reactor can be achieved in a few hours.

However, despite those obvious advantages, the H.V.E.M. cannot be used with confidence unless all the experimental variables have been understood and standardised to give reproducible results in different specimens. In the five or six years that High Voltage microscopes have been in use, much consideration has been paid by various researchers to the experimental variables, but it is difficult to compare loop densities or growth rates measured in the same metals by experimentalists in different laboratories. Indeed, many important conclusions seem to be drawn from a few measurements from a single specimen, which though self consistent are hardly representative. For these reasons, a critical analysis was carried out, on the effects of microscope variables on the subsequent radiation damage that formed. It was only possible to obtain fully reproducible results under stringent experimental conditions. The optimization of these conditions and the elimination of systematic errors are described in this chapter.

6.2 Measurement of Foil Thickness

This parameter is one of the most important variables in quantitative radiation damage work, while being one of the most difficult to measure easily or accurately. Normal methods of measuring it include

the use of slip traces or dislocation lines imaged at different beam directions. However in good H.V.E.M. specimens these are not present, so that other methods have to be used.

It is possible to calculate the thickness of a foil at any one point by counting the number of thickness fringes from the edge of the crystal. In bright field micrographs white fringes occur at t/w_g^w = 0,1,2 etc.

where t = foil thickness

w_g^w = effective extinction distance given by $\xi_g^w = \xi_g/(1+w^2)^{\frac{1}{2}}$

where ξ_g is the time extinction distance at the exact Bragg angle and w is the deviation from the Bragg angle. When w = 0 fringes occur at simple multiples of ξ_g and the thickness can be measured to an accuracy limited only by the accuracy of the calculation of extinction distance. The extinction distance for a <111> reflection in pure copper is $\simeq$ 242 Å at 100 keV and when corrected for relativistic effects is $\simeq$ 340 Å at 300 keV.

In the experimental work performed in this thesis, all thickness measurements were made at this voltage. The extinction distance of 340 Å only applies to pure copper and will be modified slightly by the presence of the aluminium solute. However a comparison of thickness measurements made using stereo pairs in conjunction with thickness fringes indicated that ξ_g = 340 Å could be accepted with a tolerance of between 5 - 10%. In general, irradiations were made exactly on a thickness contour and if large areas had to be measured a rectangular section was used, parallel with a region of constant thickness. Great care was also taken in establishing the 'two beam' conditions necessary for thickness measurement, because any significant deviation from w = 0 will result in a large error in the extinction distance.

Specimens were considered as acceptable for irradiation only if they were bend free and had large thin flat areas. Significant errors can be introduced when thickness contours in bent specimens are measured

or if there is a large difference in foil thickness across the irradiated area. The maximum error measured in thickness experiments was ≃ 10%, but in most cases a confidence of ± 100 Å in 2500 Å thick foils was achieved. If for example a foil has a thickness of 2400 ± 200 Å, a generation rate $g = 3.9 \times 10^{19}$ cm^{-3} and a measured area of 3 cm. x 3 cm. at 36,000 magnification, a total loop density of 600 loops will yield a corrected density of 3.16×10^{16} cm^{-3}. Upper and lower limits of density using t = 2200 Å and 2600 Å are 3.57×10^{16} cm^{-3} and 2.82×10^{16} cm^{-3}. The maximum error involved in this typical density measurement would be $3.16 \pm .34 \times 10^{16}$ cm^{-3}, while a more reasonable figure would be $3.16 \pm .23 \times 10^{16}$ cm^{-3}. In order to obtain consistent results irradiation of many areas on the same specimen was carried out along the same thickness fringe.

6.3 Loop Counting Procedure

Only specimens which were substantially flat over large areas were used, so that several comparable regions could be used for irradiation at different temperatures. To minimise the effects of annealing, irradiations in a given specimen were always begun at the highest temperatures to be used. The optimum time of irradiation was chosen to be that at which all defects have become sufficiently large to be observed and counted but not so large as to obscure each other, and before too many have been lost by slippage to the foil surface.

Considerable care has to be exercized when counting the number of loops on any micrograph. At very high temperatures, a low density of loops occur, giving rise to a large statistical error. There was however no difficulty in the actual loop counting as each could be observed, whether in or out of contrast. At the other extreme, irradiation of Cu/Al foils at low temperatures reduces the statistical error, but increases the error due to the overlapping of images. At these temperatures, it was also very difficult to decide which loops were in

or out of contrast, for a given reflection.

At loop densities in excess of 4×10^{16} cm^{-3}, normal high resolution bright field techniques were abandoned and stereo weak beam imaging conditions used. However, even with these techniques, an upper limit of density measurement in electron irradiated specimens appeared to be $\triangleq 10^{17}$ cm^{-3}. When the loop density was high, the image overlap caused the measured density to be lower than it should be, by as much as 10%. Corrections were made to the density measurements by using the Chute-Napier formula (Chapter 8). Alternatively, thinner foils can be used for loop density measurements at the lower temperatures since correction factors can be applied (Chapter 7) to make the observed densities comparable with 'bulk' densities.

Experimental results suggest that foil thicknesses down to $\triangleq$ 1000 Å can be used with confidence and satisfactory results were obtained when stereo density measurements from thick areas were compared to densities calculated from single micrographs taken of damage in thin foils. In order to increase the accuracy of the density results, weak beam images were taken, but care was taken in the correct interpretation since the contrast from small loops can appear as two dots, which could easily be taken for two defects Jenkins (1973). The visibility of small clusters also depends on their geometry. Thus if Frank defects are imaged in a {220} reflection in the plane of the foil, one of the three sets of inclined loops appear to show very little contrast. Jenkins concluded that if care is taken, not to strongly excite non-systematic reflections, the number and apparent sizes of defects of size >50 Å were found not to be strongly dependent on the precise diffraction conditions. His suggestion that weak beam images can give good measurements of number densities at first sight appears to be at variance with the experimental results of Haussermann (1973), whose computed images show depth oscillation of contrast for loops <50 Å in size. Haussermann concluded

that since the intensity and extent of the contrast were depth dependent, the measurements of number densities and defect size distributions by a simple counting and measuring procedure may lead to serious errors.

It is likely that depth oscillation effects may be important for very small defects located near the surface of the foil, as in ion damaged specimens. Jenkins (1973), in ion irradiated silver, where the defect sizes were >50 Å found no depth oscillations, even when the defects were situated near the top surface of the foil. In electron irradiated foils, the defects were >50 Å in size and situated at least 300 Å from each surface. Thus beam divergency smooths out depth oscillations, so that depth variations in defect visibility are not expected. Consistent results were obtained using semi 'weak beam' images measured on high magnification prints, though in many cases slightly lower densities than normal were obtained as a result of overlapping images, but this effect can be reduced using progressively larger deviations from the Bragg condition. In true weak beam images ($s = 2 \times 10^{-2}$ Å^{-1}) measurements were made by counting all the loops present whether in or out of contrast.

A further reason for counting all the loops, is that there appears to be a marked asymmetry in the distribution of $b = \frac{a}{2}\langle 110\rangle$ loops on the various {110}planes. If there were an equal number of loops on all the planes, imaging the loops in g <111> strong beam diffraction vectors would require a multiplying factor of two, to take into account the 'out of contrast' loops. Experimental measurements made on the distribution of loops, indicated that in $g = [1\bar{1}\bar{1}]$, 53% of loops were observed. In g $[\bar{1}\bar{1}1]$ 40% of all loops were observed, while g $[\bar{1}1\bar{1}]$ puts into contrast 61% of all possible loops. If for example $g = [\bar{1}1\bar{1}]$ is used to count perfect loops distributed asymmetrically on the various {110} planes, then doubling the number of 'in contrast' loops results in a loop density that is too high. Thus, if there are 1000 loops in an area

3 cm. x 3 cm. at 36,000 Mag. with a generation rate $g = 3.9 \times 10^{19}$ $cm^{-3}.sec.^{-1}$ and $t = 2400$ Å the real value of corrected loop density is 4.3×10^{16} $cm.^{-3}$. A diffraction vector g $[\bar{1}\bar{1}1]$ will indicate 3.72×10^{16} $cm.^{-3}$, while g = $[\bar{1}1\bar{1}]$ gives a loop density of 4.79×10^{16} $cm.^{-3}$. If the specific nature of the diffraction vector is unknown, then the error in loop density arising from this effect is, for the conditions given $4.3 \pm .5 \times 10^{16}$ cm^{-3}. The difficulty in applying multiplying factors of 1.92 for g $[1\bar{1}\bar{1}]$, 2.5 for g $[\bar{1}\bar{1}1]$ and 1.64 for g $[\bar{1}1\bar{1}]$ lies in the lack of information concerning loops asymmetries at low irradiation temperatures. The results obtained and discussed above were measured at irradiation temperatures of $\triangleq 200^{\circ}C$.

Significant errors may also be introduced when measuring loop densities of a mixed population of Frank or perfect loops. Measurements of loops irradiated at elevated temperatures in copper and copper aluminium alloys, indicate a gradual changeover in loop population from predominantly Frank loops in pure copper, to rhombus loops in alloys of Cu 2% Al and above. When the defects were imaged using g <111> diffraction vectors at temperatures above 180°C, the exact nature of the loops could be determined, but as the temperature of irradiation was reduced, faulted loops could not be easily distinguished from perfect loops, without extensive contrast experiments. The assumption that the ratio of Frank loops to total population is the same at high temperatures may be invalid. The presence of a mixed population of loops may explain the spurious result in Spring et al. (1971), for which the Cu .01% Be loop density was measured to be higher than the Cu .1% Be result. Micrographs in that paper certainly indicate that a mixed loop population existed, though no mention of any correction factors to account for this were given. A similar factor must be applied when measuring loops in molybdenum, Niebel (1974), in which loops of both types $b = \frac{a}{2}$ <110> and $b = \frac{a}{2}$ <111> were present.

A combination of weak beam images taken using different diffraction vectors and stereo pairs were employed in the measurement of very high loop densities, while the lower loop densities were measured using high magnification bright field micrographs in conjunction with correction factors to take into account mixed populations of Frank and perfect loops and the asymmetry of the perfect loops on the {110} planes. All the results plotted in chapter 7 were calculated using an average of many different results from various specimens, but irradiated under the same conditions.

6.4 Specimen Polish Conditions

Buswell (1974) suggested that hydrogen can be introduced into specimens during the electrolytic polishing process, which can subsequently enhance the nucleation of voids in certain stainless steels. Experiments carried out, revealed that hydrogen diffusion into copper aluminium specimens can increase the observed loop density from 10^{15} cm.$^{-3}$ to as much as 5×10^{16} cm.$^{-3}$, for irradiation under the same conditions. Quite obviously, unless special precautions are taken, hydrogen gases could influence the loop densities to such an extent that any quantitative measurements would be meaningless.

The rate of diffusion of hydrogen into the specimens is influenced by the rate of removal of the metal surface layer. A reduction of polishing temperature to about -70 or -75°C together with a high polishing voltage was found (Chapter 5.5) to reduce the amount of gas in the specimens to negligible amounts and at the same time provide very good specimens for electron microscopy work. However, this procedure can be very time consuming, so as an alternative, specimens were standardized by an in-situ anneal for 10 minutes at 380°C prior to irradiation. Specimens subjected to this treatment, or polished at very low temperatures were found to give consistent and reproducible results.

6.5 Crystal Growth Rate

Segregation effects in copper aluminium crystals appear to have a profound effect on the subsequent H.V.E.M. irradiation damage structure. Copper aluminium crystals of concentrations >2 at.% Al grown using the Bridgeman technique at speeds of 2.2 cm/hour, with a temperature gradient of $\triangleq 30^{\circ}C$/cm, tended to nucleate a mixture of Frank and perfect loops during irradiation fig. 6/1(a). The loop density was also not reproducible from one specimen to another. Quantitative experiments were not carried out to find the reason for this effect, though an electron probe analysis of the aluminium concentration of a crystal of nominal concentration 10% Al revealed that the actual percentage of aluminium was $\triangleq$ 10.5 at.%. Further, weak beam images of the Shockley/stair-rod dissociation reaction of a Frank loop in a specimen cut from the analysed crystal revealed that the average separation of dislocations was $\triangleq$ 100 Å, in this alloy.

Even though the crystals were annealed in vacuo at $1000^{\circ}C$ for long periods of time, no visible change in the damage structure occurred. A new set of copper aluminium crystals were grown at speeds down to 3 mm/hour and results from foils cut from these crystals fig. 6/1(b) indicated that in general, only perfect loops nucleate and grow as a result of electron irradiation in alloys >2 at.% Al and that Frank growth in these alloys was a phenomenon associated with fast grown crystals. Thus all density measurements of loops in copper aluminium alloys were made using slow grown crystals and fairly reproducible results were obtained from different specimens of the same alloy, irradiated under the same conditions.

6.6 Specimen Temperature

Ipohorski and Spring (1969) observed large faulted Frank loops in pure copper irradiated at room temperature, while other observers including Makin (1968) indicated that room temperature irradiations of

copper produce a very high number of small Frank loops. Recently Fisher (1970), Leighly (1974) calculated the temperature rise in thin metallic foils as a function of beam energy, diameter, flux, specimen density, thickness and atomic number using the corrected Bethe electron energy loss formula for relativistic electrons. Their results suggest that in materials of high thermal conductivity the temperature rise will be small even for high electron fluxes, provided that the beam diameter at the foil is small and the latter is adequately supported.

Experiments with copper aluminium foils revealed that inadequate clamping of specimens could result in temperature rises in the specimen by as much as 50^{o} - 100^{o}C, and thus great care was taken to ensure good thermal contact between the specimen and the molybdenum furnace of the hot stage, by using a spring loaded tungsten circlip. It was also important however, not to deform the specimen by clamping too tightly.

A double tilt, water cooled hot stage designed and built by Donaghay and Rushton was used for all the irradiation experiments. This stage had the advantage that the thermocouple measured the temperature very near the specimen. Stage drift, by radiative heat transfer to the holder was almost completely eliminated. A further characteristic of this stage, was that specimen temperatures could be quickly and accurately adjusted to a tolerance of $<5^{o}$C using thermocouple readings. Once set, the temperature did not drift under normal irradiation conditions. No observable temperature rise of the specimen was recorded during irradiation at a low dose rate of 6×10^{18} el./cm^2/sec. (.5 μA in a 12.5 μm diameter spot), even though the beam diameter was large. However, at higher dose rates of 2×10^{20} el./cm^2/sec., considerable beam heating by as much as 100^{o}C was recorded. Great care was taken especially in the formation of voids to ensure that the bias and condenser 2 were set so that beam heating did not occur. Beam shapes and temperature rises in foils were also examined as a function of bias and C_2 setting by

Buswell, Makin (1973). It is clear that in a specimen undergoing electron irradiation, a radial temperature gradient exists between the centre of the irradiation area and the surrounding material; the magnitude of this gradient depending on the beam profile and intensity, thermal conductivity of specimen and the manner in which it is mounted.

The possibility of an axial temperature gradient was considered when in some foils stereo measurements of loop distributions yielded a marked asymmetry in the depth profiles. It was thought that this may have originated from an increase in the rate of energy loss from the electron beam, with an increase in penetration distance, but calculations Bethe (1933) showed that the rate of change of energy loss from an electron beam of initial energy 1 MeV, passing through an H.V.E.M. foil was insufficient to produce a detectable temperature gradient. In the relativistic region the Bethe-Bloch expression for the energy loss becomes:-

$$-\frac{dE}{dX} = .153\rho \left(\frac{Z}{A}\right) \beta^{-2} \left\{ \log_{\varepsilon} \left[\frac{E(E+MC^2)^2\beta^2}{2I^2MC^2} \right] + (1-\beta^2) \right.$$

$$\left. - (2 - \sqrt{1-\beta^2} - 1+\beta^2) \log_{\varepsilon} 2 + \frac{1}{8} (1 - \sqrt{1-\beta^2})^2 \right\}$$

where $\beta = {}^{v}/_{c}$, I = excitation energy, ρ = density. If values representative of a 3000 Å thick copper foil are substituted into the expression the energy loss is calculated to be $\simeq$ 400 eV for electron energies of 1 MeV.

When the objective aperture was removed during the irradiation of a specimen at dose rates $>10^{19}$ el/cm^2/sec a temperature reduction was observed and recorded by the thermocouple as being $\simeq 20^{o} - 40^{o}$C. The presence of the objective aperture caused the lower part of the specimen to be hotter than the upper part, with the consequence that there was a continuous variation of loop densities across the foil thickness. Stereo measurements of radiation damage produced under these conditions revealed a marked asymmetry and reduction of loop density at the electron

exit surface. However, damage as a result of irradiation at 6×10^{18} $el/cm^2/sec.$ exhibited no such effects and no detectable temperature rise was observed, as the aperture was inserted. It seems likely that during high dose rate irradiations for void formation, the objective aperture should be removed, or inserted only to correct for specimen drift. If this is not done, void or loop densities recorded will be unrepresentative of that temperature.

The temperature rise of the specimen caused by the electron beam can be estimated using an equation proposed by Fisher (1970)

$$(T_m - T_o) = \frac{I_o \, \Delta E \, a^2}{4Kd} \{\nu_o + \log_\varepsilon (b/a)^2\}$$

where I_o = specimen beam flux

$\frac{\Delta E}{d}$ = energy loss in thin foil

b = conductor radius

a = beam radius

ν_o = Eulers constant

K = Thermal conductivity

The temperature rise of a copper specimen using the above formula was computed for two beam profiles; profile (A) Bias 1 C_2 = 1 generation rate $g = 2 \times 10^{20}$ $cm^{-3}sec^{-1}$ was estimated to increase the foil temperature by about 60^oC, while profile (B) bias 4 C_2 = 12 generation rate $g = 3 \times 10^{19}$ $cm^{-3}sec^{-1}$, used in normal density measurements was calculated to increase the foil temperature by $\simeq 3^oC$. These magnitudes of temperature rise were recorded by the thermocouple. Since an increase in irradiated area can be accompanied by a marked temperature rise, initial scanning of large areas of the specimen in the search for suitable areas was always carried out at very low flux densities and with electron energies below the threshold i.e. 300 keV.

6.7 Beam Profile

Since the electron flux ϕ varies across the diameter of the beam

a knowledge of current density as a function of position in the beam was required. Measurements can be made either by collecting the beam on an insulated viewing screen or by use of a Faraday cup. By inserting an intermediate aperture, the current in a small area can be obtained, and hence the beam profile. Alternatively the total current in the beam can be measured and the profile found by recording the beam photographically and scanning the area with a microdensitometer. Observations indicate that the beam profile is approximately Gaussian of the form

$$\phi = \phi_o \exp\left(-\frac{r^2}{s^2}\right)$$

where ϕ = flux at the beam centre

r = distance from the beam centre

s = effective beam radius.

If the beam profile is not adjusted correctly, steep damage gradients exist across the irradiated area giving false values of loop density for a given generation rate. However, a compromise must be reached, between the increase in beam diameter to give a flat topped profile and the temperature rise that inevitably occurred when the beam diameter was increased. For loop density measurements, a beam flux of .5 μA in a 12.5 μm diameter spot was found to be an acceptable compromise, with negligible beam heating or damage gradients. At the magnifications used, 25 or 40 K, the size of the photographed area was 3 - 4 μm to give a uniform generation rate over the area under investigation.

Ipohorski (1969) reported that large variations of beam current at the specimen can occur, without noticeable effect on the viewing screen. If this does occur, then the generation rate can change to alter significantly the loop growth parameters. As part of this thesis was concerned with loop growth the possible beam instability was checked by passing the current to earth through a high stability resistor, the

voltage being displayed on a digital voltmeter. Over a period of two hours, little change was observed in the beam current.

It was also found important in quantitative radiation damage experiments to keep the filament batteries fully charged at all times, otherwise irregular beam profiles occurred.

6.8 Specimen Contamination and Microscope Vacuum

Contamination occurs by the decomposition of organic molecules, absorbed on the specimen in dynamic equilibrium with the concentration in the microscope vacuum. While Bahr (1966) has demonstrated that contamination can be reduced at high voltages, it is still significant enough to stress the foil and alter the radiation damage network. Contamination can however be reduced by use of a cold finger operating at liquid nitrogen temperature, which lowers the partial pressure of organic molecules in the specimen area. If the nitrogen trap is allowed to dry up, a layer can be observed to agglomerate on the specimen surface with the consequence that impurities may be knocked into the specimen. Loops can also slip to the surface as a result of specimen stress.

The effects of contamination can clearly be observed in the work reported by Spring et al. (1971), in which measured values of loop densities in pure copper were very much lower than the densities in Cu .01% Be. The micrographs also show slip traces, indicative of a contamination layer, while the scatter of loop densities as a function of irradiation temperature was very large. The experimenters used different specimens to obtain the results and it is possible that the variation in density may be explained if the copper specimens had different amounts of contamination on the foil surface.

The microscope vacuum is a variable that has not been recorded in experimental work published in the literature even though it can fluctuate considerably from experiment to experiment. Significant changes were observed in the vacuum conditions if a dirty specimen holder was inserted or if 'wet plates' were loaded in the camera.

The range of vacuum conditions recorded at the specimen chamber of the Oxford H.V.E.M. ranged from 2×10^{-4} torr. to 3×10^{-5} torr. Loop density measurements for this thesis were generally made when the vacuum was $\simeq 6 \times 10^{-5}$ torr. At present, quantitative experimental evidence has not been obtained as to the effect of microscope vacuum on radiation damage, though it was observed that an increase in contamination rate occurred as the vacuum worsened. Increased ion damage also occurred, which could only be eliminated by conditioning the microscope at frequent intervals. Irradiations were normally performed at 900 keV, rather than 1 MeV in order to reduce the effect of ion damage in the foils, and the microscope was conditioned at 1100 keV, after each 1½ hours of irradiation. When this procedure was not carried out regularly, spurious radiation damage effects in the form of ion damage were visible. The ion densities in some foils were as high as 4×10^{14} cm^{-3}, with some clusters being 500 - 1000 Å in size. Quite frequently holes were knocked completely through the foil in thin areas. The onset of ion damage can easily be distinguished from normal electron damage, in that the clusters were very irregular. It is quite possible that some void swelling results reported in the literature using the H.V.E.M. have been influenced by ions. However, if suitable precautions are made, it is not thought to be a serious problem.

6.9 Damage Cross Section

In this thesis defect generation rates have been calculated using a displacement rate of 19 eV. for pure copper, which at an electron energy of 900 keV gives a displacement cross section for damage of 75 barns. The loop density results were self-consistent, because two beam g <111> conditions were used at a <532> beam direction for all the irradiations relating to loop density measurements. In real terms however, the results may be in error for two reasons:-

(1) Impurity atoms can alter the threshold damage significantly.

The threshold damage voltage for pure copper was calculated to be ≃ 400 keV by Makin (1968) while that of the solute aluminium is ≃ 166 keV, Wolfenden (1972). Thus it appears likely that threshold voltages for copper aluminium alloys may be lower than that for pure copper, thus increasing the displacement cross-section and generation rate.

(2) Threshold energies are orientation dependent and vary significantly, when the irradiation direction is changed from <111> to <110> or <100>.

Since precise measurements of threshold voltage have not been measured for irradiation along the <532> direction Makin's value was used as being representative of this direction.

Electron channelling has also been observed to alter the defect density by as much as 1.7 times, Thomas (1971) and so the deviation from the Bragg condition was kept constant for all the irradiations.

6.10 Magnification Calibration

The magnification of the H.V.E.M. cannot be determined to an accuracy of more than 5% due to specimen height variations or objective lens current changes. Even the expansion or contraction of films or prints can alter the final magnification. A diffraction grating was used to calibrate the magnification of the microscope and as far as possible, micrographs were taken under the same experimental conditions.

6.11 Specimen Quality

Since the H.V.E.M. was used to inject damage into the foils, it was essential that all specimens were standardised to ensure consistent results. Methods of eliminating residual hydrogen gas have already been discussed and a method of producing low dislocation densities in the unirradiated foils was mentioned in Chapter 2. Dislocations act as biased sinks for interstitials and any dislocations present can alter the observed loop density significantly.

The specimen must also be free of the electrolytically produced

viscous layer which results from the polish treatment and rigorous procedures were adopted for cleansing the specimens before they were inserted into the microscope.

Stress caused by bending was mainly a problem associated with the preparation of copper specimens and these were handled with extreme care by vacuum tweezers. Any foils with the slightest degree of bending were discarded.

In conclusion, when all the precautions mentioned in this chapter were adopted and used, consistent results were obtained, not only from a single specimen, but from many specimens cut from the same crystal.

CHAPTER 7

Application of the Brown, Kelly, Mayer (BKM) Theory to the Clustering of Radiation Damage Loops in Copper Aluminium Alloys

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7.1 Introduction

The early T.E.M. observations of electron radiation damage in metals were carried out using Van der Graaf accelerators, which were limited by their low dose rate of $\simeq 10^{13}$ el/cm^2/sec. This limitation was removed by the introduction of the High Voltage Microscope which could generate dose rates of $10^{18} - 10^{21}$ el/cm^2/sec and allow in-situ observations at the same time. Consequently, a large amount of experimental data has been accumulated over the last seven years, particularly in F.C.C. metals.

Since the initial defect damage is accumulated in the form of Frenkel pairs, it is possible to relate the subsequent damage to the recovery stages observed by resistivity or quenching experiments.

The first H.V.E.M. studies of displacement damage in metals were carried out by Makin (1968), who irradiated copper and aluminium thin foils with electron beams of energies 1000 keV at room temperature. In this experiment, small dislocation loops in the form of black spots were observed early in the irradiation, characteristic of a situation in which the vacancy diffusion rate was small. No new loops were observed to nucleate after the initial stage. Makin also noticed a denuded zone at grain boundaries and specimen surfaces, which was estimated to be $\simeq$ 1000 Å. Extensive jogging of dislocations was also noticed.

A similar formation of loops was observed in Cobalt by Howe (1970), Nickel by Bourret (1971) and Urban (1971), Iron by Thomas (1969), Gold by Rualt (1972) and copper Ipohorski (1969). Urban (1971) showed that they were formed by agglomeration of interstitial atoms. The denuded zone at each surface in nickel foils at room temperature was measured by Urban to be $\simeq$ 150 Å, in comparison to $\simeq$ 600 Å for copper specimens at this temperature. Thus the conventional technique of determining the nature of loops in copper using stereo images and relating the depth of the defect to the direction of black white contrast cannot be used

because of the depth at which the defects are situated.

The fact that precipitates can lose coherency during irradiation Woolhouse (1971) provided evidence that, at ambient temperatures, the migration of free interstitials is the major controlling factor in damage production. The effect of impurities and pre-existing dislocations have also been examined at room temperature by Wolfenden (1972), who found it difficult to produce visible damage in impure aluminium, but in high purity aluminium doped with helium, black spot damage was experienced at electron energies less than the calculated threshold. This sub-threshold damage was attributed to electron displaced helium atoms, which were then able to displace aluminium atoms in a two step mechanism. When black spot damage became visible close to a dislocation, Stobbs (1973) interpreted this as being due to the enhanced interstitial clustering caused by the dislocation strain field.

Experiments were carried out at temperatures < stage I_E by Urban (1972), who irradiated nickel with 650 keV electrons at $8^{o}K$ in an H.V.E.M. fitted with a helium cold stage. Dot like images as a result of strain around point defect aggregates were observed after a dose of 5×10^{20} el/cm^2 and it was proposed that since long range defect migration was not possible at these temperatures, the aggregates formed as a result of statistical effects, which become predominant at high point defect concentrations, Luck and Sizmann 1964 (A) and (B). Urban (1974) (1975) also reported experimental observations on lead and copper at irradiation temperatures between 8 and $300^{o}K$.

Bourret (1968) who irradiated zone refined nickel in a Van der Graaf accelerator with 2 and 3 MeV electrons in the temperature range 233 - $283^{o}K$ with subsequent examination at $293^{o}K$, found that interstitials had aggregated to form Frank loops, but no evidence of vacancy clusters was observed in contrast to Urban's results from iron (1972). Bourret also calculated the defect retention ratio to be $\simeq 10^{-3}$, a result which he

attributed to the recombination of interstitials with immobile vacancies or the presence of submicroscopic clusters.

Bourret (1971) and Urban (1971) carried out further experiments on H.V.M. irradiated Nickel and though both results agreed generally with the earlier accelerator data, Bourret observed only Frank loops while Urban observed a mixture of Frank and perfect loops, attributed to surface stress induced loop unfaulting. Bourret also reported that an increase in impurity level resulted in a marked increase in loop density and a decrease in loop size, in agreement with earlier observations by Shimomura (1969) who investigated loop concentrations and average loop diameters in 5N and 6N gold irradiated with 3 MeV electrons at 130°K. The loop density in the impure gold was observed to be $\simeq 5 \times 10^{16}$ cm.$^{-3}$ while that in the 6N gold $\simeq 9 \times 10^{14}$ cm.$^{-3}$, indicating that the influence of impurities on cluster density in gold is very significant.

Experiments have also been performed by Ipohorski and Spring (1969) (1970) on thin copper foils irradiated with 650 keV electrons. The subsequent damage formed at 20°C (large faulted Frank loops) was representative of damage normally formed at 200°C. It is likely that beam heating of the specimen caused a temperature rise. They also observed small stacking fault tetrahedra in copper doped with silicon and beryllium, consistent with observations on quenched metals in which impurities appear to promote the formation of these defects.

Spring et al (1971) investigated the effect that alloying up to 2 at.% Be with copper had on the loop densities and concluded that the interstitial migration energy in copper is .12 ± .03 eV. The binding energy between an interstitial and a beryllium atom was also measured as .29 ± .07 eV. They concluded that the effect of the foil surfaces must be taken into account, by using a correction factor such as that proposed by Coringe (1971), for the migration of mobile interstitials to the foil surfaces.

Chen et al (1973) using a 200 keV microscope, investigated cluster production and loop growth rates in electron irradiated aluminium. The free interstitial migration and interstitial impurity binding energies were measured to be $\simeq$ .06 eV and $\simeq$ .4 eV respectively. A considerable orientation dependence of damage was observed (when using the same Bragg conditions), which they attributed to changes in the point defect production rate caused by Bloch wave channelling. Maximum damage rates were observed at exact low index orientations <100>, <111>, with a sharp drop by a factor of 3 when the crystal was tilted a few degrees away. These results indicated a clear need for consistency in choice of the exact crystal orientation and diffraction conditions in any systematic experiment. Hossain (1973) (1974) investigated the radiation damage at elevated temperatures in Ni and Ni-Si alloys, in which the migration energy of a self interstitial in nickel was estimated to be .21 $\pm$ .05 eV and the interstitial silicon binding energy as .32 $\pm$ .08 eV.

A review of the Japanese work on this subject was given by Kiritani (1975), in which results of observations on Al, Au, Cu, Fe, Ni, Mo, Pt and W were presented. The trapping of interstitials by foreign atoms was discussed and the vacancy migration energy in copper measured (from loop growth rates) as $\simeq$ .6 eV.

In spite of the large amount of effort expended over the last few years, the diffusion characteristics of interstitial point defects in metals are still not understood. The question which has not been resolved concerns the temperature range over which interstitials become mobile and in particular, whether interstitials migrate in stage 3. A major problem encountered in the study of interstitials stems from the fact that it is not possible to produce them in the absence of vacancies. Electron irradiation damage results have to be treated with caution in view of the possible statistical aggregations of point defects which occur at high concentrations. However, when only one type of cluster

is observed, it suggests that diffusion of the associated defect has occurred, implying that loops form as a result of long range interstitial diffusion. When irradiated specimens are annealed at temperatures within the recovery stage 3, the fine distribution of interstitial loops decrease both in loop size and concentration until they disappear on completion of the recovery. A basic interpretation of this observation is that the interstitial loops are annihilated as a result of long range vacancy migration.

7.2 B.K.M. Theory of Loop Nucleation

If vacancies are assumed to be immobile, the clustering of interstitials occurs either by homogeneous nucleation involving the chance collision of migrating interstitials, or by heterogeneous nucleation involving the meeting of migrating interstitials with another interstitial bound to an impurity atom. Either process can be described by the chemical reaction rate theory, the simplest assumption being that the di-interstitial is immobile and forms a stable nucleus B.K.M. (1969) Makin (1969). As vacancies are assumed immobile, the steady state is not reached and C_V (the vacancy concentration) continues to grow, although not indefinitely, since saturation will eventually reduce the effective defect creation rate. A newly formed defect then has a high probability of being formed close to an existing vacancy and of being annihilated.

In homogeneous nucleation, an interstitial migrates at a jump rate given by

$$\nu_I = \nu_o \exp\left(\frac{S_I^m}{k}\right) \exp\left(-\frac{E_I^m}{kT}\right) \qquad (1)$$

until it achieves one of the following reactions (a) annihilation with a vacancy (b) trapping by another interstitial (c) annihilation at the edge of the loop. Each of these processes compete for interstitials. At the beginning of the irradiation processes (a) and (b) predominate,

whereas at the end of the irradiation, when there are a large number of sinks for interstitials, the interstitial concentration falls and processes (a) and (c) predominate. It is thus possible to think of a nucleation stage in which the loops are nucleated and a growth stage during which no more are nucleated and those present merely grow. These assumptions lead to quantitative predictions of cluster density 1^{∞} given by Makin as

$$1^{\infty} = \sqrt{\frac{K}{5.4\ \alpha_R \nu_I \Omega^2}}\ \text{cm.}^{-3} \qquad (2)$$

where K = defect generation rate

α_R = number of sites around a defect for recombination

ν_I = interstitial jump rate

Ω = atomic volume

The second alternative is heterogeneous nucleation in which the preceding theory can be applied, but with the modification that the migration rate of interstitials is effectively reduced by an amount depending on the time bound to an impurity atom. Brown et al. (1969) suggested that this leads to a cluster density greater than that given by equation (2). They modified the chemical reaction rate theory proposed by Woolley (1963), by including differential equations formulated to allow for the variation of loop density and average loop radius with time. The theory also takes into account the modification to the interstitial velocity by impurity trapping.

The major reason for the formation of interstitial loops at temperatures 300 - 400°K, lies in the extraordinarily high mobility of interstitials, compared to the vacancy mobility of $\simeq .1$ jumps/sec. The effect of the migration of vacancies can therefore reasonably be neglected at the early stage of irradiation. Since the vacancy activation energy in copper aluminium alloys is higher than that of copper, vacancy mobility

will be delayed to higher temperatures. Calculations by Hossain (1974) with vacancy mobility built into the B.K.M. equations concluded that this parameter does not have a significant effect on the nucleation stage of radiation damage.

The B.K.M. theory predicts that the number of interstitial loops reaches a limiting value shortly after irradiation commences and that the saturation number per unit volume when aluminium is present is given by:-

$$1^{\infty} = 2.9 \left[\frac{G}{\bar{s}\Omega}\right]^{\frac{1}{2}} \tag{3}$$

where G = generation rate

Ω = atomic volume

$\bar{s}$ = average velocity of an interstitial atom.

$$\bar{s} = \frac{s}{1 + \frac{1}{2} s\Omega n_b t_o} \tag{4}$$

and n_b = impurity concentration

$$t_o = \nu^{-1} \exp (E_m + E_b)/kT \tag{5}$$

Substituting

$$s = \gamma a \nu \exp (-\frac{E_m}{kT}) \tag{6}$$

$$1^{\infty} = 2.9\ g^{\frac{1}{2}} \left[\frac{1}{\gamma a \nu \Omega} \exp (\frac{E_m}{kT}) + \frac{1}{2}\frac{n_b}{\nu} \exp\left(\frac{E_m + E_b}{kT}\right)\right]^{\frac{1}{2}} \tag{7}$$

where E_m = interstitial activation energy

E_b = binding energy of interstitial to impurity.

For intrinsic behaviour

$$\frac{1}{\gamma a \Omega \nu} \exp (\frac{E_m}{kT}) \geq \frac{1}{2}\frac{n_b}{\nu} \exp\left(\frac{E_m + E_b}{kT}\right) \tag{8}$$

i.e. if

$$\gamma a \Omega n_b \exp\left(\frac{E_b}{kT}\right) \leq 2$$

then

$$\ln.(l^{\infty}) = \ln. 2.9 + \frac{1}{2} \ln.g - \frac{1}{2} \ln. (\gamma a \Omega \nu) + \frac{E_m}{2kT} \qquad (9)$$

It follows that the slope of a plot $\ln.(l^{\infty})$ v $\frac{1}{T}$ should be $E_m/2k$. If the inequality is reversed, the extrinsic or impurity controlled behaviour results. The slope of $\ln.(l^{\infty})$ v $\frac{1}{T}$ then gives $(E_m+E_b)/2k$ and at constant temperature $l^{\infty} \propto n_b^{\frac{1}{2}}$.

Experiments were undertaken to obtain quantitative data on the combined effects of the aluminium concentration and irradiation temperature on the subsequent loop density and these results compared with the theoretical predictions presented by Brown et al. (1969). Before these precise measurements were carried out, considerable time was spent in quantifying the effects of the variables that cause error in the radiation damage results. These were discussed in chapter 6. Extreme care was taken in establishing the irradiation conditions, so that the experimental results could be treated with confidence. Much of the radiation damage (especially at high loop densities) was examined in a 100 keV microscope, which offered the advantage of greater resolution and stability compared with the H.V.E.M.

Fig. 7/1 illustrates the loop density measurements observed in an irradiated foil of Cu 16% Al. The following parameters were used in all the experiments

defect generation rate $g = 3.79 \times 10^{19}$ cm.$^{-3}$ sec.$^{-1}$

beam direction $\bar{z} = \langle 532 \rangle$

diffraction vector $\bar{g} = \langle 111 \rangle$

thickness $h = 6\xi_g$ (300 keV)

All specimens annealed in-situ for 5 minutes at 380°C prior to irradiation.

Graph (B) shows the measured densities at the foil centre as a function of temperature, without taking into account correction for the specimen foil surfaces. A change of gradient can be observed at about 180°C, below which loop densities are very high and linear as a function of temperature. The loop densities rapidly decreased to zero at 300°C for the foil thicknesses used.

Goringe (1971) modified the B.K.M. theory using Fourier expansions of all the quantities involved and included a diffusion parameter P in the interstitial concentration equation. The results indicate that most observations of loop densities reported in the literature require considerable correction for surface effects. The nucleation equation proposed by B.K.M. for the interstitial concentration was given by

$$\frac{di}{dt} = g - \frac{1}{2}\Omega ivs - 2\sqrt{2}\,\Omega i^2 s - \frac{8}{3\sqrt{3}}\Omega \bar{r} lis \qquad (10)$$

where i = interstitial concentration

v = vacancy concentration

l = loop density

s = interstitial speed

$\bar{r}$ = loop radius, defined as zero for a di-interstitial.

If the quantities i, v, l, r are written as Fourier series of the form

$$c(t) = \sum_q c_q(t) \sin\left(\frac{\pi q z}{h}\right) \qquad (11)$$

which is the solution of the one dimensional diffusion equation

$$\frac{\partial c}{\partial t} = P \frac{\partial^2 c}{\partial z^2} \qquad (12)$$

with boundary conditions c = 0 at z = 0 and h then adding a surface diffusion term of the form

$$\frac{\partial c_q(t)}{\partial t} = -\frac{P\pi^2 q^2}{h^2} c_q(t) \qquad (13)$$

to equation (10), multiplying through by sin $(\frac{\pi q z}{h})$ and integrating, we obtain

$$\frac{di_q}{dt} = g_q - \frac{\Omega}{2} i_j v_k M_{jkq} s - 2\sqrt{2}\,\Omega i_j i_k M_{jkq} s \qquad (14)$$

$$- \frac{4\Omega}{3\sqrt{3}\pi a} i_j c_k M_{jkq} s - q^2 P i_q$$

where M_{jkq} is a numerical factor.

The following dimensionless quantities were defined by Goringe:-

$$I_q = i_q \sqrt{\frac{\Omega s}{g}} \qquad V_q = v_q \sqrt{\frac{\Omega s}{g}}$$

$$I_q = 1_q \sqrt{\frac{\Omega s}{g}} \qquad C_q = \frac{c_q}{a} \qquad R = \frac{r}{a} \qquad \theta = t\sqrt{\Omega s g}$$

$$G_q = \frac{g_q}{g} \text{ and } P = \frac{P\pi^2}{h^2\sqrt{gs\Omega}} \qquad (15)$$

Equation (14) now becomes

$$\frac{dI_q}{d\theta} = G_q - \frac{1}{2} I_j V_k M_{jkq} - 2\sqrt{2}\, I_j I_k M_{jkq} - \frac{4}{3\sqrt{3}\pi} I_j C_k M_{jkq} - q^2 P I_q \qquad (16)$$

The vacancy concentration, loop concentration and loop size can be expressed in a similar form, resulting in a set of linear first order differential equations for the time dependence of the q^{th} Fourier components. The meaning of the terms in equation (16) is as follows:- The rate of increase in the interstitial concentration is given by the generation of interstitials G_q less their loss by (1) recombination with vacancies $\frac{1}{2} I_j V_k M_{jkq}$ (2) the formation of new interstitial loops $2\,2\, I_j I_k M_{jkq}$ (3) attachment to the dislocation line circumscribing existing loops $^4/3\sqrt{3}\pi\ I_j C_k M_{jkq}$ (4) diffusion to the foil surface $q^2 P I_q$. The parameter

$$P = \frac{as\pi^2}{h^2\sqrt{gs\Omega}}$$

in equation (16) was used, to apply a correction to measured loop densities, either at the foil centre or averaged throughout the total foil thickness. The variables a and Ω in the above equation have been defined to be 2.55×10^{-8} cm and 1.5×10^{-15} cm^2 respectively.

The interstitial velocity s can be calculated from

$$1^{\infty} = 2.9\sqrt{\frac{g}{s\Omega}}$$

once the loop density has been measured, then substituted in the equation

$$P = \frac{as\pi^2}{h^2\sqrt{gs\Omega}},$$

to find P. For moderately large values of P ($10^2 - 10^4$), which were those normally experienced in thin foil measurements, the straight line portion of fig. 7/2 yields an analytic expression for the corrected value P_c of $P_c = \sqrt{7.3P}$. If mean densities are measured, $P_c = \sqrt{4.2P}$. Fig. 7/2 was derived by Goringe (1971) and is included here for completeness. Once the corrected value of P has been obtained, the ratios $\frac{1 \text{ centre}}{1 \text{ bulk}}$ or $\frac{1 \text{ mean}}{1 \text{ bulk}}$ yield the bulk loop densities.

Graph (A) fig. 7/1 represents the loop densities of curve (B) corrected to bulk. Two points were immediately apparent:- (1) The loop densities were boosted upwards by a factor of 10 at room temperature and 100 at high temperature. (2) The gradient of the uncorrected density curve was much steeper than that of the bulk density curve, demonstrating that, unless corrections for the foil surfaces are made, the activation energies deduced, even from a self-consistent set of experimental results may be markedly in error.

The accuracy of this correction was checked by irradiating a Cu 16% Al specimen at different thicknesses in the same foil, at a

temperature of 210°C. Fig. 7/3 shows the corrected and uncorrected loop densities as a function of thickness, measured by counting extinction fringes. Even in the region of rapidly changing measured densities 500 - 2500 Å, the corrected densities all tended to adopt the bulk value of $\simeq 10^{16}/cm.^3$, indicating that up to 3000 Å, foil thickness has little effect on the final corrected bulk value. Rather unexpectedly, the measured loop density saturated at $\simeq 8 \times 10^{14}$ $cm.^{-3}$ (when foils of thickness >3000 Å were being irradiated) instead of tending towards the bulk value, as predicted by fig. 7/2. The saturation was not caused by statistical errors, image overlap or inaccuracies in thickness measurement. At present, no explanation can be proposed for this phenomenon, though it seems likely that whatever causes the asymmetry in loop plane distribution as a function of depth fig. 11/1(b) also causes the reduction of loop density in foils >3000 Å thick.

There has recently been much discussion in the literature concerning foil thicknesses to be used for H.V.E.M. specimens, in order to simulate 'bulk' conditions. The arguments mainly centre round the H.V.E.M. as an instrument for examining and producing voids as an alternative technique to ion or neutron irradiation. Many papers suggest 5000 Å or even 10,000 Å as the foil thickness to achieve this objective, though results from loop density measurements made in Cu 16% Al suggest that these values may be optimistic. If the observed interstitial loop density is not representative of bulk, then the void densities arising from those dislocation loops are likely to be incorrect.

Fig. 7/4 illustrates the relationship between loop density and diffusion parameter P. When both the bulk and loop density at the foil centre were plotted, both were observed to become equal when P = 1, at a loop density of $\simeq 10^{18}$ $cm.^{-3}$ for the foil thicknesses used in the experiment. However, loop densities of $>10^{17}$ $cm.^{-3}$ are impossible to measure accurately in the microscope due to the image overlap, so it

seems likely that bulk conditions will not easily be obtained in copper aluminium foils. Fig. 7/5 shows the theoretical relationship between the loop density at the foil centre and foil thickness in order to obtain bulk values. When P was set equal to one, for a given foil thickness and generation rate, the interstitial velocity and hence the loop density could be calculated. It seems clear from fig. 7/5 that either very high loop densities must be measured or that very thick foils must be irradiated.

Fig. 7/6 shows loop density measurements in zone refined copper as a function of irradiation temperature and for comparison, results obtained by Spring et al (1971) from copper corrected to take into account the difference in the generation rates between the two experiments. The significant difference in loop density between the two results were attributed to the slippage of loops to the foil surface caused by contamination in Spring's foils. The activation energy for the migration of interstitials deduced from the gradient $E_m/2k$ of fig. 7/6 was .13 ± .02 eV.

The formula

$$1^{\infty} = 2.9\ g\ \frac{1}{2}\ \{\frac{1}{a\Omega\nu}\ \exp\ (\frac{E_m}{kT})\}^{\frac{1}{2}}$$

was used to calculate the theoretically expected densities when activation energies of E_m = .13 and .14 eV were substituted. The best agreement between calculation and experimental results was obtained with $\nu = 1.1 \times 10^{13}$ sec^{-1} and 1.5×10^{13} sec^{-1} respectively and are plotted in fig. 7/6. These values of vibration frequency, ν, agree very well with the commonly accepted value of $\simeq 10^{13}$ sec^{-1}. The loop behaviour followed the normal pattern for copper, in that at room temperature, a high density of small Frank loops was observed, while an increase of temperature caused a gradual reduction in loop density, but an increase in loop size. At a temperature of about 180°C, the loop density dropped very rapidly to

reach zero at temperatures in excess of 220°C for a foil thickness of ≃ 2400 Å. Since vacancy mobility does not affect the loop density, the likely cause is that the di-interstitial is not stable in this temperature range Bourret (1970). An analysis of the activation energy involved in the di-interstitial dissociation is given later in this chapter. The results for pure copper indicate that the di-interstitial is stable at temperatures below 180°C and that the B.K.M. theory with suitable choice of variables can explain the experimental results. Error bars have not been added, because the maximum error (in absolute terms) that could occur would render any claims to a measurable activation energy, impossible. The accuracy with which the densities have been measured is indicated by the closeness with which the experimental points follow the theoretical curve and a claim of ±.02 eV seems reasonable under the circumstances.

Fig. 7/6 also illustrates the measured loop densities in a Cu .98% Al specimen and these are slightly higher than the densities in a pure copper foil. Intrinsic behaviour was again observed, together with an activation energy for interstitial migration of .13 - .14 eV. The loop densities were not so easily measurable in this alloy, or in the dilute alloys Cu .077% Al, Cu .15% Al or Cu .31% Al because the loop population contained a mixture of Frank and perfect loops. The Cu .98% Al alloy was irradiated to find out whether an intrinsic to extrinsic nucleation transition existed in the temperature range under investigation. Basically, the Cu .98% Al specimens behaved in a manner similar to that of pure copper, with the exception that only 10% of the loops were Frank. Results of experimental determinations of loop densities in the more dilute alloys have not been included, because a precise relationship between the ratio of Frank loop population to total loop population could not be established at the lower temperatures, thus making accurate loop density measurements difficult to obtain.

Fig. 7/7 illustrates the magnitude of the loop densities observed

in a Cu 2% Al specimen, in which only rhombus perfect loops were observed. Preliminary experimental results indicated that a linear relationship between $\log_{10} 1^{\infty}$ and $\frac{1}{T}$ was not occurring, consistent with a change of intrinsic to extrinsic nucleation behaviour. According to the B.K.M. theory, this is calculated as

$$a\Omega n \exp\left(\frac{E_b}{kT}\right) \simeq 2$$

$$\therefore T \simeq \frac{E_b}{k \ln\left(\frac{2}{a\Omega n}\right)}$$

Calculations of the transition temperature T for Cu/Al foils were made with values E_b .10, .11 eV and .12 eV. (E_b was measured to be $\simeq$ .11 eV from loop densities in concentrated Cu/Al alloys) which show that such a transition should only be visible in the alloys Cu .98,2 and 5. Al, for the temperatures and binding energies under investigation. In Cu 5% Al however, the dissociation of the di-interstitial modified the observed loop densities, so that any transition at $\simeq 225^{\circ}C$ was washed out. In Cu .98% Al no change of gradient from intrinsic to extrinsic behaviour was observed, because the transition calculated for a binding energy of .11 eV occurred at $\simeq 36^{\circ}C$. This was not detectable within the scope of the present experiments. An extension of the work, using a cold stage would be necessary before any quantitative conclusions could be made concerning the behaviour of loop nucleation in this alloy.

The transition from intrinsic to extrinsic behaviour was calculated to lie in the range 70 - 135°C, with E_b = .10 - .12 eV for the Cu 2% Al alloy. Four specimens of this alloy were examined and two separate irradiations carried out on each, with particular attention paid to the temperature range 20°C - 160°C. Though conditions were adjusted as far as possible to be the same in each irradiation, the results showed a slight scatter, but the general trend was that a linear behaviour was not being

observed. Instead a gradual change was observed. It is possible to associate the low temperature irradiation with impurity controlled behaviour and the high temperature irradiation with intrinsic nucleation.

Values of the various parameters were substituted in the equation:-

$$1^{\infty} = 2.9\, g^{\frac{1}{2}} \left\{ \frac{1}{a\Omega\nu} \exp\left(\frac{E_m}{kT}\right) + \frac{n}{2\nu} \exp\left(\frac{E_m + E_b}{kT}\right) \right\}^{\frac{1}{2}}$$

with ν = vibration frequency as a variable parameter in order to obtain the best agreement with the experimental results. The effect of changing ν can be seen in fig. 7/8, in which values of 5×10^{12}, 7×10^{12} and 10^{13} sec^{-1} were used. Quite a considerable influence was exerted on the final loop density, as ν was changed, though the gradients were similar. The best theoretical agreement was achieved when $\nu = 8.5 \times 10^{12}$ $sec.^{-1}$, $E_m + E_b = .24$ eV and $E_m = .12$ eV. The calculations quite clearly demonstrate a curved appearance, in common with the experimental observations. A small deviation was observed at room temperature and at 140°C, but these come within the experimental inaccuracies of the measurements.

Results obtained from irradiation of Cu 5% Al foils are shown in fig. 7/8 and illustrate the effects that residual gas introduced by the electropolish can have on loop densities. The graph summarizes the results from several specimens, each given different prior irradiation treatments.

(A) Polished - 50°C 5.2 V. No anneal.

(B) Polished -45°C 4.4 V. No anneal. First irradiation at 240°C.

(C) Specimens, given 5 mins. anneal at 380°C.

(D) Polished - 50°C 5.2 V, then annealed for 8 minutes at 290°C.

In general, it was very difficult to evaluate the effect hydrogen has on loop densities, since the concentration was unknown and once in the specimen, could diffuse out again at a rate dependent on the specimen

temperature, thickness and alloy concentration. Prior to the recognition that hydrogen gas could diffuse into the specimens, non reproducible loop densities were measured, whose value depended on the exact polish conditions. Several irradiations of a thin foil under identical conditions also produced a diminishing number of dislocation loops.

Fig. 7/9 shows a typical reduction in loop density that occurred in a foil of Cu 16% Al electropolished at - 35°C, 4.4 volts. The initial high loop density of 2.63×10^{16} cm^{-3} was typical of hydrogen doped specimens after irradiation at 240°C. Further irradiations of the same specimen in different areas along the same thickness contour at 240°C produced a loop density diminishing quite rapidly as a function of time, but tending towards a density of $\simeq 2.7 \times 10^{15}$ cm^{-3} representative of low temperature polished foils. This graph demonstrates the importance of using standard degassed specimens before quantitative irradiation experiments are performed.

Fig. 7/8 clearly shows that hydrogen can influence the nucleation of loops by at least a factor of 10, the effects being most apparent at temperatures in excess of 125°C. The hydrogen atom appears to prevent the dissociation of the di-interstitial at high temperatures and also causes additional damage by being knocked on into the lattice to displace copper atoms in a two stage process.

The results indicate that the loop nucleation behaviour was impurity controlled throughout the temperature range, but the gradient measured from fig. 7/8 gave $(E_m+E_b) \simeq .23$. Substitution of these activation energies in equation:-

$$1^{\infty} = 2.9\, g^{\frac{1}{2}} \left\{ \frac{i}{a\Omega\nu} \exp\left(\frac{E_m}{kT}\right) + \frac{n}{2\nu} \exp\left(\frac{E_m+E_b}{kT}\right) \right\}^{\frac{1}{2}} \qquad (17)$$

did not give agreement with the experimental observations. However, the activation energy of .23 eV was calculated on the assumption that

the gradient was $\frac{(E_m+E_b)}{2k}$, which implied that:-

$$a\Omega n \exp\left(\frac{E_b}{kT}\right) >> 2$$

and

$$\frac{1}{an\nu} \exp\left(\frac{E_m}{kT}\right) = 0$$

so that

$$1^{\infty} = 2.9\, g^{\frac{1}{2}} \left\{ \frac{n}{2\nu} \exp \frac{E_m+E_b}{kT} \right\}^{\frac{1}{2}} \qquad (18)$$

When the activation energies were substituted in the equations for 1^{∞}, the resultant loop densities were so different as to suggest that at this aluminium concentration the inequality

$$a\Omega n \exp\left(\frac{E_b}{kT}\right) >> 2$$

was not being satisfied.

When the parameters E_m+E_b = .24 eV, E_m = .13 eV and $\nu = 5 \times 10^{12}$ sec^{-1} were substituted in equation (17), good agreement was obtained with the experimental results though the gradient measured from the graph gave E_m+E_b = .23 eV. In fact the gradient of the theoretical curve was not quite a linear function of $\frac{1}{T}$ at high temperatures as a consequence of the inequality $a\Omega n \exp(E_b/KT) >> 2$ not being completely satisfied.

The results for the alloy Cu 16% Al are shown in fig. 7/10. Since the densities were exceptionally high, most of the experimental points were plotted using an average figure from many runs. Weak beam stereo micrographs were also taken using a 100 keV microscope, so that overlapping of images could be eliminated. As in the Cu 5% Al alloy, the activation energy (E_m+E_b) from the experimental results was .01 eV lower than the value required to be substituted in equation (17) to give the 'best fit'. It can also be observed that the theoretical values of loop density derived from eqn. (17) are linear as a function of temperature,

in comparison to the results in Cu 5% Al, where a distinct curve could be observed. Thus for Cu 16% Al the inequality $a\Omega n \exp(E_b/kT) >> 2$ is true. The parameters substituted to obtain the best agreement of experimental and theoretical results for Cu 16% Al were $\nu = 4.7 \times 10^{12}$ sec^{-1}, $E_m + E_b = .24$ eV and $E_m = .13$ eV.

The temperature dependence of ν can be evaluated in the impurity controlled region by plotting loop density l^{∞} against impurity concentration $n^{\frac{1}{2}}$. With equation (17) and $a\Omega n \exp(E_b/kT) > 2$

$$\frac{dl^{\infty}}{dn^{\frac{1}{2}}} = 2.9 \left(\frac{g}{2\nu}\right)^{\frac{1}{2}} \exp\left(\frac{E_m + E_b}{2kT}\right) \qquad (19)$$

Fig. 7/11 demonstrates the relationship of l^{∞} to $n^{\frac{1}{2}}$ and measurement of the gradient gives $\nu = 3.95 \times 10^{12}$ sec^{-1} at $T = 293^{\circ}K$ and $\nu = 4.82 \times 10^{12}$ sec^{-1} at $T = 393^{\circ}K$. This is in good agreement with values of ν obtained from measurements of impurity controlled alloys when

$$\frac{1}{a\Omega\nu} \exp \frac{E_m}{kT} = 0$$

7.3 Measurement of Interstitial Velocity

The effect of the foil surfaces, was to reduce the loop density well below that of the bulk material and to increase the measured interstitial velocity. This followed directly from Browns formula $l^{\infty} = 2.9 (g/s\Omega)^{\frac{1}{2}}$. Without correction for diffusion to the foil surfaces, the range of interstitial velocities measured in Cu 16% Al for example was between 1.34×10^{3} cm/sec at room temperature and 1.34×10^{9} cm/sec at 260°C. When the loop densities were corrected, to simulate 'bulk' values then the interstitial velocity at room temperature was 33 cm/sec and 6.31×10^{4} cm/sec at 240°C.

Fig. 7/12 illustrates the change of corrected interstitial velocity, as a function of irradiation temperature and alloy concentration. For a given temperature, the interstitial velocity in zone refined copper was

a factor of 15 times the velocity in Cu 16% Al. The activation energies correspond to the migration of interstitial atoms, through the trapping and detrapping by impurity atoms, which is typically the activation energy to release an interstitial atom from the impurity. The trapping of interstitials by impurities accelerates the interstitial cluster nucleation and causes a reduction of measured interstitial velocity as a function of alloy concentration. Fig. 7/12 shows that the effective speeds of migration of interstitials were different in the alloys, as a result of the different number of trapping centres, but the temperature dependence of the migration speed was the same, reflecting the same activation energy to release the interstitials from the impurities. This applied only to impurity controlled loop nucleation. The graph also demonstrates the effect residual hydrogen gas has on the interstitial velocity. Large amounts of gas appear to trap the interstitials causing loop nucleation sites to grow and effectively reduce the velocity. When the gas diffuses out of the specimen, less trapping occurs and the interstitial velocity increases. Curve (A) was obtained from a specimen annealed for 8 minutes at 280°C prior to irradiation, while curves (C) and (D) were typical of those specimens given no anneal before the irradiation.

The interstitial speed was given by B.K.M. (1969) as

$$\bar{S} = \frac{S}{1+\frac{1}{2}S\Omega n t_o}$$

where

$$S = a\nu \exp\left(-\frac{E_m}{kT}\right)$$

and

$$t_o = \nu^{-1} \exp \frac{E_m + E_b}{kT}$$

Substituting these values into the equation for $\bar{S}$

$$\bar{S} = \frac{a\nu \exp\left(-\frac{E_m}{kT}\right)}{1 + \frac{1}{2} a\Omega n \exp\left(\frac{E_b}{kT}\right)}$$

then

$$\ln\sqrt{S} = \frac{1}{2}\ln(a\nu) - \frac{1}{2}\frac{E_m}{kT} - \frac{1}{2}\ln\left[1 + \frac{1}{2} a\Omega n \exp\left(\frac{E_b}{kT}\right)\right]$$

and

$$\frac{d(\ln\sqrt{S})}{d(\frac{1}{T})} = -\frac{E_m}{2k} - \frac{1}{2}\left[\frac{\frac{1}{2} a\Omega n \left(\frac{E_b}{k}\right) \exp\left(\frac{E_b}{kT}\right)}{1 + \frac{1}{2} a\Omega n \exp\left(\frac{E_b}{kT}\right)}\right] \qquad (20)$$

If the inequality $\frac{1}{2} na\Omega \exp(E_b/kT) >> 1$

$$\text{ie } ns\Omega t_o >> 2$$

then equation (20) becomes

$$\frac{d(\ln\sqrt{S})}{d(\frac{1}{T})} = -\frac{E_m}{2k} - \frac{E_b}{2k}$$

$$= -\frac{(E_m + E_b)}{2k} \qquad (21)$$

however if the inequality is reversed then

$$\frac{d(\ln\sqrt{S})}{d(\frac{1}{T})} = -\frac{E_m}{2k} \qquad (22)$$

While these inequalities were not strictly satisfied, the errors involved can be ignored to a first approximation. Fig. 7/13 shows the experimental validity of equations (21) and (22).

The interstitial speed equation also transforms to

$$\frac{d \ln\sqrt{S}}{dn} = -\frac{1}{2}\frac{\frac{1}{2} a\Omega \exp\left(\frac{E_b}{kT}\right)}{1 + \frac{1}{2} a\Omega n \exp\left(\frac{E_b}{kT}\right)}$$

which, for $ns\Omega t_o >> 2$ gives

$$\frac{d \ln\sqrt{S}}{dn} = -\frac{1}{2n}$$

i.e.

$$\frac{d(\ln\sqrt{S})}{d(\ln.n)} = -\frac{1}{2} \qquad (23)$$

This relationship was satisfied at temperatures in the range 20°C to 180°C. The B.K.M. equation (17) predicts that in the impurity controlled region the loop density α (impurity concentration)$^{\frac{1}{2}}$. This was only strictly true when

$$\frac{n}{2\nu} \exp\left(\frac{E_m+E_b}{kT}\right) >> \frac{1}{a\Omega\nu} \exp\left(\frac{E_m}{kT}\right)$$

In the case of Cu 2% Al and Cu 5% Al, a small error in loop density resulted if the right hand term was set equal to zero. However, for all practical irradiation experiments this can be ignored, since on a log scale, the error in loop density for Cu 2% Al was ±.03 and ±.02 for Cu 5% Al.

Fig. 7/14 shows the relationship between loop density and alloy concentration.

Three distinct regions were observed:-

(a) loop density not impurity controlled,

(b) transition from intrinsic to extrinsic behaviour,

(c) impurity dominated nucleation.

The loop density for pure copper appears to be higher than one might expect from the graph, and this may be due to the presence of various impurities. The kink in the graph at point (b), may be due to the difficulty in distinguishing Frank and rhombus loops at room temperature in the Cu 98% Al alloy specimen. However, despite these inaccuracies, the graph verifies the B.K.M. prediction that $l^{\infty} \propto n^{\frac{1}{2}}$, in Cu/Al alloys for the temperature range 20° - 200°C.

7.4 Dissociation of the di-interstitial

All the results so far indicate that the B.K.M. assumption of a mobile interstitial and an immobile di-interstitial acting as a stable nucleus for loop growth is true. Equation (17) predicts that $l^{\infty} \propto g^{\frac{1}{2}}$ where g - generation rate of defects. This relationship was verified for copper and Cu 10% Al at low irradiation temperatures. Fig. 7/15 shows the results of plotting loop density generation rate, for a Cu 10% Al foil during irradiation at T = 110°C. Three distinct regions could be distinguished on the graph. At high dose rates (c) the loop density tended to saturate, probably as a result of irradiation induced temperature rises in the foil either directly or reflected from the objective aperture. Since great care was taken in loop measurement, the possibility of loop image overlap was discounted. Thus any loop density measurements made at high dose rates were liable to be well below the predicted density for a given temperature and dose rate. In region (B), the relationship $l^{\infty} \propto g^{\frac{1}{2}}$ was verified and the results suggest that for copper aluminium alloys consistent results may be obtained with irradiation dose rates in the range 2×10^{18} el/cm^2/sec to 2×10^{19} el/cm^2/sec. At low dose rates region (A), there was some deviation from the $g^{\frac{1}{2}}$ curve, which could not be attributed to statistical error. At those dose rates, it was hardly possible to observe any damage on the screen, due to the low electron intensities. Thus the times of irradiation were 10 to 15 times those of the higher dose rates where the loops could be easily imaged. The most likely reason for the apparent saturation in loop density was that continuous nucleation was occurring at impurities. This behaviour was observed many times in specimens of high alloy concentration during irradiation at elevated temperature.

Similar experiments were attempted in a Cu 16% Al alloy at 215°C (the region of rapidly changing density as a function of temperature) but due to the variability of the results, no quantitative conclusions

could be drawn for the relationship between loop density and generation rate at high irradiation temperatures.

At high temperatures, the B.K.M. assumption of a stable di-interstitial nucleus, breaks down. Hossain (1974) has performed theoretical calculations using the B.K.M. theory, but with the vacancy assumed to be mobile. Vacancy mobility had little effect on loop densities, though this was expected since the loops are nucleated very early on in the irradiation and there will not be a sufficient number of vacancies to affect the nucleation. Results from loop growth experiments indicate that while vacancy mobility in copper can occur at $\simeq 50^{o}C$, the vacancies will not be mobile in Cu 16% Al until very much higher temperatures, (chapter 10).

Other possible modes of nucleation in electron irradiated metals are:-

(1) The interstitial and di-interstitial mobile and a tri-interstitial forming a stable nucleus. According to B.K.M. $1^{\infty} \propto (g/\Omega s)^{n}/2$ for a nucleus of size (n+1) interstitials. Thus when n = 1 (a di-interstitial nucleus) the observed $g^{\frac{1}{2}}$ relationship is predicted. If a tri-interstitial acts as the nucleus, n = 2 and $1^{\infty} \propto g$. This behaviour has not been observed over any temperature range.

(2) The interstitial and di-interstitial are mobile, but dissociation of the di-interstitial can occur. The tri-interstitial acts as a stable nucleus and according to Bourret (1970), when this occurs $1^{\infty} \propto g^{5/6}$. Attempts to measure this relationship at high temperatures were not successful, probably as a result of beam heating in the foil at high dose rates.

(3) Nucleation occurring on an impurity. In this situation, $i_2 n$ is the stable nucleus. This case has been discussed by B.K.M. and applies to copper aluminium alloys of concentration >2 at.% Al.

(4) Nucleation occurs on an impurity with the di-interstitial

unstable.

When the di-interstitial is unstable, Bourret (1970) has calculated the loop density to be:-

$$l^{\infty}_{\text{unstable}} \simeq l^{\infty}\ (\text{B.K.M.})\ \beta^{-2/3} \tag{24}$$

where

$$\beta = \left(\frac{\nu}{G}\right)^{\frac{1}{2}} \exp\left(-\frac{E_m+2E_{ii}}{2kT}\right) \tag{25}$$

and E_{ii} = di-interstitial binding energy.

If $\beta \ll 1$, the loop concentration is the same as predicted by B.K.M. The di-interstitial binding energy E_{ii} calculated to give the observed loop density transition at $\simeq 180^{\circ}C$ is $\simeq .65$ eV, with parameters

$G = 4.5 \times 10^{-4}\ \text{sec}^{-1}$

$E_m = .13$ eV

$\nu = 10^{13}\ \text{sec}^{-1}$

substituted in equation (25). The new equation for loop density becomes:-

$$l^{\infty} = 2.9\ g^{\frac{1}{2}}\left\{\frac{1}{a\Omega\nu}\exp\frac{E_m}{kT} + \frac{n}{2\nu}\exp\frac{E_m+E_b}{kT}\right\}^{\frac{1}{2}}\left(\frac{\nu}{gV}\right)^{-1/3}\exp\left(\frac{E_m+2E_{ii}}{3kT}\right) \tag{26}$$

The defect creation rate G used by Bourret (1970) has been replaced by gV where g = generation rate and V = atomic volume.

Equation (26) becomes:-

$$l^{\infty} = 2.9\left(\frac{g}{\nu}\right)^{5/6}\left(\frac{1}{V}\right)^{-1/3}\left\{\frac{1}{a\Omega}\exp\frac{5E_m+4E_{ii}}{3kT} + \frac{n}{2}\exp\frac{5E_m+3E_b+4E_{ii}}{3kT}\right\}^{\frac{1}{2}} \tag{27}$$

where the parameters have their usual meanings.

The dependence of l^{∞} on g (generation rate) now increases to the $^{5}/_{6}$ power and if nucleation is intrinsic, the gradient of a plot of $\ln(l^{\infty})$v $\frac{1}{T}$

will be

$$\frac{5E_m+4E_{ii}}{6k}.$$

When nucleation is impurity controlled the first term can be set to zero and the gradient will be

$$\frac{5E_m+3E_b+4E_{ii}}{6k}.$$

As with the calculations for the low temperature irradiations, the inequality was not large enough to justify setting

$$\frac{1}{a\Omega}\exp\frac{5E_m+4E_{ii}}{3kT} = 0$$

and in order to obtain agreement between experimental and calculated results, equation (27) was used.

No theoretical comparisons have been made with experimental results in pure copper, because loops could not be formed in sufficient numbers at the temperatures where the di-interstitial becomes unstable. In Cu2, 5 and 16% Al alloys, a pronounced change in loop densities occurred at $\simeq 180^{\circ}C$ which was easily measurable. When values $E_m = .13$ eV, $E_b = .11$ eV and $\nu = 4.7 \times 10^{12}$ sec^{-1}, the theoretical results agreed with experimental data in Cu 16% Al specimens when $E_{ii} = .65$ eV. The gradient measured from the graph, of .63 eV, differed slightly from the .65 eV calculated using equation (27) in that the first term of equation (27) was set equal to zero and the measured gradient equated to

$$\frac{5E_m+3E_b+4E_{ii}}{6k}$$

Equation (27) was also used to calculate loop densities at high temperatures in Cu 2 and Cu 5% Al and the experimental and calculated results were found to agree when

$$\nu = 8.5 \times 10^{12} \text{ sec}^{-1} \quad E_{ii} = .68 \text{ eV}$$

and

$$\nu = 5 \times 10^{12} \text{ sec}^{-1} \quad E_{ii} = .66 \text{ eV}$$

respectively. For consistent results, both the Bourret and B.K.M. formulations have to be used as a whole unless n or E_b are very high. First approximations can be obtained of the di-interstitial binding energy, if the high temperature loop density v reciprocal temperature gradient is equated to

$$\frac{5E_m+4E_{ii}}{6k} \text{ or } \frac{5E_m+3E_b+4E_{ii}}{6k}$$

depending on whether nucleation is intrinsic or extrinsic.

An order of magnitude calculation of the di-interstitial binding energy can be obtained by considering the elastic strain energy of a loop with 1 or 2 atoms. According to Hossain (1974)

$$E(n) = \frac{\mu b^{3/2} v^{1/2} n^{1/2}}{2\pi^{\frac{1}{2}}(1-\nu)} \ln \frac{16\, n^{\frac{1}{2}}}{\pi^{\frac{1}{2}} e}$$

with v = atomic volume 1.21×10^{-32}

$\bar{b}$ = Burgers vector 2.5×10^{-8}

μ = shear modulus 7.56×10^{11}

ν = Poissons ratio .42

Substituting the values for pure copper

$$E(1) = 3.805 \text{ eV and } E(2) = 6.92$$

Since the di-interstitial binding energy

$$E_{ii} = 2E(1) - E(2)$$

then

$$E_{ii} \simeq .69 \text{ eV}$$

The values of E_{ii} obtained from the experimental results at high temperatures are in agreement with the above estimate.

These results must be treated with caution for two reasons:-

(1) The correction factor proposed by Goringe has been calculated on the assumption that the di-interstitial is the stable nucleus. It is quite possible that different corrections may be required if

calculations are performed on the assumption that the di-interstitial is unstable. Even though the results of fig. 7/3 demonstrate that similar bulk densities can be obtained whatever the foil thickness at a temperature of 215°C, there is no evidence to suggest that the 'bulk' values derived are in fact real values, since correction factors relating to a stable di-interstitial nucleus have been applied to a situation where it is presumed that the di-interstitial is unstable. Calculations are at present being carried out by Mr. D. Imeson (private communication) to extend the B.K.M. theory by taking into account not only the foil surfaces, but vacancy mobility and an unstable di-interstitial.

(2) The correction factor proposed by Bourret

$$\beta^{-2/3} = \left(\frac{\nu}{G}\right)^{-1/3} \exp \frac{E_m + 2E_{ii}}{2kT}$$

does not reflect a change in transition temperature on the impurity binding energy E_b. Fig. 7/13 indicates that the transition temperature was constant, possibly because $E_b < 2E_{ii}$ or because it is independent of alloy concentration.

Figs. 7/16 and 7/17 illustrate the dependence of loop density on irradiation temperature and solute concentration at constant temperature. The micrographs demonstrate clearly the reduction in loop density as the temperature was increased and the increase of loop density as the alloy concentration was increased. As the binding energy E_b was low in Cu/Al, the loop density dependence on alloy was not so pronounced as it was for Cu/Be Spring et al. (1971) where $E_b \triangleq .29$ eV or in Ni-Si alloys Hossain (1973) where $E_b \triangleq .32$ eV.

The calculations made by Hayns (1974) appear to be in conflict with the observation of a drop in loop density at high temperatures, which was attributed to di-interstitial dissociation. In his rate theory calculations he allowed the thermal dissociation of a di-atom pair with an

activation energy β by formulating differential equations that included a dissociation probability proportional to $e^{-\beta/kT}$ and the appropriate addition of two single atoms to the interstitial population. When values of β were chosen as .3, .4 and .5 eV, the change in total loop concentration was found to be small. However, his calculations assumed low values of β and other parameters pertinent to stainless steel. At present, no loop density results have been published for stainless steel, so it is not possible to tell whether Hayns prediction for this metal is true.

7.5 Investigation into the Thickness of the Surface Denuded Layer

The surfaces of thin foils are obviously important sinks for point defects created by the irradiation and their effects on the loop densities and swelling have been considered by a number of authors including Makin (1968), Brown et al. (1969) and Goringe (1971). Inclusion of the foil surfaces in the rate equations, means that vacancy and interstitial concentrations must be considered as functions of the depth x in the foil. The terms

$$D_v \frac{\partial^2 C_v}{\partial x^2} \quad \text{and} \quad D_i \frac{\partial^2 C_i}{\partial x^2}$$

describe the diffusion of vacancies and interstitials to the surface. The spatial boundary conditions on C_v and C_i are $C_v = C_i = 0$ at $x = 0$, the foil surface and $dC_v/dx = dC_i/dx = 0$ at $x = h/2$, the foil centre. Results of the diffusion calculations carried out by Goringe indicate that no clear cut definition of a so called 'denuded zone' exists, because for large values of diffusion parameter P (thin foils, high irradiation temperatures) the loop density throughout the foil is reduced from its bulk value. Fig. 7/18 illustrates the loop density as a function of depth for various values of P from calculations by Goringe. In H.V.E.M. irradiation experiments, the smallest P value achieved was ≃ 20 and the depth profiles indicate that a semi-denuded zone exists completely

across the foil.

The term denuded layer is commonly used to describe the region near the surface where cluster formation is completely suppressed. Generally, a gradual reduction in loop density was observed near the foil surfaces (to an extent dependent on the irradiation parameters) instead of a precise cut off and for the purposes of this thesis, the denuded zone has been arbitrarily defined as the zone adjacent to the surface, containing $\simeq$ 5% of the total number of loops.

Makin (1968) has estimated the width of the layer denuded of loops near the surfaces or grain boundaries as

$$x = \frac{\nu_i \lambda^2}{KV}^{\frac{1}{2}}$$

where λ = jump distance 2.55×10^{-8} cm

ν_i = interstitial jump rate

$= \nu_o \exp^{-E_m/kT}$

K = generation rate 3.79×10^{19} cm^{-3} sec^{-1}

V = (loop density)$^{-1}$

It was assumed that E_m for copper $\simeq$ .2 eV, to give $\nu_i = 4.5 \times 10^9$ sec^{-1} at room temperature and a value of denuded zone width of 1210 Å.

Application of this formula to results obtained in pure copper for this thesis, indicates that the denuded zone width covers the whole specimen. The loop density measured in copper at 300°K, was 1.1×10^{15} cm^{-3}, which with a generation rate 3.79×10^{19} cm^{-3} sec^{-1}, E_m = .12 eV and $\nu_i = 6.55 \times 10^{10}$ sec^{-1} give an estimated denuded width of $\simeq$ 3516 Å.

Brown has also examined the concept of denuded zone width and supposed that during nucleation, if an interstitial atom originates a certain distance from a planar sink, it has a considerable probability of reaching it and will then have originated in the 'denuded zone'. The number of jumps an interstitial makes in the nucleation time is $s/a(g\Omega s)^{\frac{1}{2}}$ and so the root mean square distance it can go in this time

is a $(s/a(g\Omega s)^{\frac{1}{2}})^{\frac{1}{2}}$. On the assumption that $\Omega = a^2$, the denuded width was estimated as $(^s/g)^{\frac{1}{4}}$. The value of denuded zone calculated in this way was observed to increase with temperature or a reduction in alloy concentration. However, even the lowest estimate of denuded zone width was much larger than the foil thickness. For example Cu 16% Al specimens at room temperature nucleated a deduced 'bulk' loop density of 7.95 x 10^{16} cm^{-3} and an interstitial velocity of 33 cm/sec.

The estimated denuded zone width was then calculated to be $\simeq$ 3070 Å implying that specimens of thickness < 6140 Å will produce no loops. However, it is possible to reconcile this answer with the minimum foil thickness to produce bulk irradiation for loop densities of 8 x 10^{16} cm^{-3}. For this bulk density, the density at the foil centre was calculated to be 1.23 x 10^{16} cm^{-3} and the measured interstitial velocity 1400 cm/sec, to give a denuded zone using $(^s/g)^{\frac{1}{4}}$ of 7714 Å. Fig. 7/6 indicates that for this loop density, a minimum foil thickness of $\simeq$ 7850 Å is required before bulk conditions are satisfied. The denuded zone widths calculated from Makins and Browns formulae refer to depths below which bulk conditions are not satisfied, since the surface acts as a significant sink not only near the surface, but for several thousand angstroms away from it. In order to decrease the value of the surface influence, thick foils, low temperatures, high activation energies, high beam currents and high accelerating voltages must be used.

Experimental measurements of 'denuded zone' have been made for Cu, Cu 5% Al and Cu 16% Al over a range of temperature 293°K to 500°K. Stereo measurements were made on loops after irradiation at a fixed dose rate 3.79 x 10^{19} cm^{-3} sec^{-1}, until they grew sufficiently large to be resolved, but not large enough to interact. Loop sizes of about 250 Å were measured at the lower temperatures, but as the temperature was increased, the loop diameters grew large, thus making a precise determination of depth more difficult. At temperatures in excess of 480°K, the

loop density was low, so that statistically the observed zone widths are dubious. The foil with a normal [111] was tilted about 8^{o} on either side of this direction and diffraction conditions g = <220> established for stereopairs. A thin layer 50 Å thick of gold was evaporated onto the specimen surface so that accurate depths could be measured using high magnification prints accurately aligned under a Hilger-Watts stereoviewer. The results are shown in fig. 7/19.

Quite clearly, the measured denuded zones of 250 Å in Cu 16% Al at room temperature do not agree with those values calculated using the B.K.M. theory. However, it is possible to obtain quite accurate estimates of denuded zone thickness by measuring the bulk density of an irradiated foil by two methods:-

(1) Measurement of mean loop densities, using the total foil thickness and then correction to bulk values.

(2) Measurement of loop densities at the foil centre, by subtracting the two denuded zones at either surface from the total foil thickness, correcting to bulk densities using correction factors and then equating the bulk densities obtained, to find the value of the denuded zone.

If the total foil thickness is h and each denuded zone width is x then the measured mean density is

$$1^{\infty}_{\text{mean}} = \frac{\text{no. of loops counted}}{\text{area h}}$$

The value of 1^{∞} was substituted into

$$S = \frac{(2.9)^2 g}{1^{\infty 2}\,\Omega}$$

to find the interstitial velocity, then

$$P = \frac{as\pi^2}{h^2\sqrt{gs\Omega}}$$

was calculated using the value of S obtained. Goringe (1971) predicted that for large P values, an analytic expression for a corrected P_c will be obtained using $P_c = \sqrt{4.2}P$. Graph fig. 7/2 was then used to obtain a value of $\frac{1 \text{ mean}}{1 \text{ bulk}}$, for which value of P_c, a value of bulk loop density was obtained. A similar procedure was carried out using the loop density at the foil centre.

$$1^{\infty}_{\text{centre}} = \frac{\text{number of loops counted}}{\text{area} \cdot (h - 2x)}$$

The value of x was treated as an adjustable parameter which was varied so that when the formula $P_c = \sqrt{7.3}P$ was used to find $\frac{1 \text{ centre}}{1 \text{ bulk}}$, the values of loop density calculated by the two methods were equal. The calculated results have been included in fig. 7/19 and agree with the experimentally observed denuded zones, suggesting that a 5% cut off for the denuded zone is a reasonable estimate.

A further effect of specimen thickness, is the possibility that defects once formed, might slip to the surface under the influence of image forces. The force required to move a screw dislocation lying in the foil plane is given by:-

$$F = \frac{\mu b^2}{2\pi} \sum_{i=1}^{\infty} \frac{x}{(2i-1)^2 (\frac{h}{2})^2 - x^2}$$

where μ = shear modulus

h = foil thickness

If this force is greater than $b\tau$, where τ = friction stress for dislocation movement, the dislocation will slip to the nearer surface. For an accuracy of 20%, terms other than the leading term can be neglected Makin (1972). The safe region in the centre of the foil from which dislocations will not slip is given by:-

$$\Delta = (A^2 + h^2)^{\frac{1}{2}} - A$$

where $A = \mu b/2\pi\tau$. Calculations of the safe regions at the foil centre for copper and copper 14% Al, indicate that screw dislocations are not stable in copper foils of $\simeq 2500$ Å. For the alloy however, the friction stress is high and dislocations are not likely to slip to the surface. The situation for glissile loops is not given by this formula, but during irradiation, loops were not observed to slip to the surface, at least in the early stages of irradiation. As the loops grew larger the diameter became as large as the foil thickness, with the consequence that slippage occurred. The safe region in which dislocations are stable, is a very important parameter when measuring void densities, since in thin foils at high dose rates and temperatures the dislocation density can be reduced in comparison to its bulk value. The denuded zone produced as a result of slippage will be superimposed on the denuded layer resulting from the diffusion of point defects to the surface. The denuded zones measured in Cu/Al foils agreed with the calculated values and indicate that slippage of loops to the surface was not a significant factor in the accurate measurement of loop densities.

7.6 Nucleation Time

Dislocation loop formation involves separate nucleation and growth stages, though the former, as a result of its short duration was very difficult to study. Makin (1968) has estimated the nucleation time as

$$\left(\frac{1}{KV}\right)$$

where K = generation rate

V = reciprocal loop density.

Application of this equation to copper foils irradiated at 300°K gave a nucleation time of $\simeq 5 \times 10^{-5}$ seconds. B.K.M. (1969) on the other hand, defined the nucleation time as $t_n = 10/\sqrt{g\Omega s}$. The predicted nucleation time was very small in all alloys and varied from 6.3×10^{-3} sec. to 10^{-4} sec, with the smallest nucleation time occurring in Cu 16% Al

foils irradiated at room temperature.

On the basis of this evidence, it is reasonable to assume that any observable increase in loop number density during the first few minutes of irradiation, cannot be considered a part of the nucleation stage. By the time the defect clusters reach a size resolvable in the microscope (10 - 20 Å), nucleation has already been completed and any further observed increase in loop density is really the result of defect clusters becoming resolvable as a result of growth rather than nucleation. Fourier diffusion calculations performed by Goringe (1971) concluded that at sufficiently large times, the asymptotic solution of the variables takes the same form as predicted by B.K.M. (on the assumption that the di-interstitial is stable and the vacancy immobile.) Thus $I_q \propto \theta^{-2/3}$, $V_q \propto \theta^{2/3}$, L_q = constant, $C_q \propto \theta^{1/3}$ and $R_q \propto \theta^{1/3}$. However, the value of θ (nucleation time) above which the asymptotic solution may be expected to hold increases rapidly with increased surface diffusion. Curves of loop density at the foil centre for small and large surface diffusion parameters as calculated by Goringe (1971) are shown in Fig. 7/20. The approach to the asymptotic solution and the depression of the loop density which followed from large surface effects is illustrated. The minimum experimental values of θ measured in the present experiments were in the range 5×10^5 to 10^6, so it is possible that the increase in loop density observed in foils irradiated at constant temperature may be an effect of the diffusion of point defects to the foil surface. According to fig. 7/20, a small increase in loop density may occur in the range of θ 10^5 to 10^7 for $P \simeq 10^3$.

Measured loop densities as a function of reduced time θ are illustrated in fig. 7/21 for pure copper and Cu 16% Al. In general, during irradiation at low temperatures, vacancies were immobile and nucleation of interstitial clusters ceased within a very short period. Curve (B) Copper, $P \simeq 40$, $T_i = 20^oC$ and curve (D) Cu 16% Al $P \simeq 30$ $T_i = 20^oC$

illustrate the observed constant density. This observation agreed with the B.K.M. theory of rapid nucleation and also with Goringe's prediction that for small values P, the asymptotic loop density will be reached after $\theta \simeq 10^5$.

At the beginning of the irradiation, interstitials and vacancies increase together linearly with irradiation time. In a very thin foil, the interstitials soon escape to the foil surfaces, remain level in concentration for a certain period and then start to decrease, when the vacancies become more effective as sinks than the surfaces. The vacancy concentration still increases. This interstitial concentration in a very thin foil is not usually high enough to nucleate observable clustered defects, though under certain conditions vacancy clusters may form. In thick foils, escape to the surface is not so effective and the accumulated vacancies become dominant sinks for interstitials. At this time, the interstitial concentration decreases, while the vacancy concentration increases. The observed early cessation of the interstitial cluster nucleation may be understood, from the existence of the appreciable concentration of interstitial atoms only at the beginning of irradiation.

At elevated temperatures ($\simeq 200^{\circ}C$), the situation may be considerably complicated due to:-

(1) vacancy mobility,

(2) heterogeneous nucleation on impurities,

(3) diffusion of point defects to the foil surfaces, delaying the approach to the asymptotic loop density. It is likely that all three factors influence the nucleation rate, though there appears to be some controversy, as to whether vacancy mobility can affect the initial increase in interstitial loop density. Hossain (1974) modified the B.K.M. theory to include vacancy mobility, but calculated that no significant change in loop density would occur. According to

Kiritani (1975) however, vacancies soon maintain the balance with interstitial atoms the steady state, when $V_v C_v = V_I C_I$, (where V_v and V_I are the mobilities of vacancies and interstitials) a constant rate of nucleation takes place.

Thus vacancy mobility affects the initial nucleation stage for both copper and Cu 16% Al. At the same time, the small increase in loop density shown in fig. 7/21 curves (A) and (C), between $\theta = 5 \times 10^5$ and 5×10^6 was also consistent with the theoretical predictions of increased nucleation time as a result of the diffusion of point defects to the foil surface. As the irradiation time was increased, the loop density in pure copper curve (A) $T_i = 210^oC$, $P \triangleq 200$ increased by a small amount. At $\theta \triangleq 10^7$, small loops of an unknown nature appeared though they did not grow very rapidly (δ), while at large values of θ, the Frank loops in the foil unfaulted to interact with other loops or with the surface resulting in a significant reduction in loop density as shown at point E. Curve (C) represents the loop density observed in a Cu 16% Al foil irradiated at $T_i = 235^o$ having a surface diffusion parameter $P \triangleq 230$. Region α shows the gradual increase in loop density similar to that observed in pure copper, while at points β and γ dislocations interacted with one another and a significant number of small loops were observed to nucleate; some of which grew while others reduced in size. The nature of these small loops was not determined.

Fig. 7/22 illustrates the change of loop density as a function of dose in more detail, for a specimen of Cu 16% Al irradiated at 235^oC, the micrographs of which are shown in fig. 7/23.

One important feature to emerge from the graph was that the total loop density at large values of θ was constant until very pronounced loop interaction occurred. In fact, the density of new loops nucleated since the early nucleation almost exactly balanced the continuous loss of loops due to slippage to the surface or interaction with other loops.

When $\theta = 10^7$, however, the rate of loop interaction greatly exceeded the rate of nucleation so that a large reduction in total loop density was observed. There also appears to be a discontinuity in the rate of nucleation of new loops when $\theta = 6.61 \times 10^6$, at which time, a very large number of new loops were nucleated. This can be related to the rapid reduction of dislocation sink density which occurred at this time.

In fig. 4/10, loops α which nucleated well after the initial nucleation stage had ended can be seen to grow to large sizes, discounting the possibility that they are all of vacancy type. Also in this micrograph; loop β shows very irregular growth, loop γ shows interaction of a loop with the foil surface and loop δ illustrates loop amalgamation. The rate of nucleation of these new loops slowed down and tended to saturate at values of θ in excess of 10^7. The difference in the density of new loops in copper and Cu 16% Al irradiated at 200°C suggests that while loss of dislocation sink densities at long irradiation times can account for a small amount of re-nucleation, it does not explain the very large densities observed in Cu 16% Al alloys. New loops in this alloy may be continuously nucleated on impurity complexes.

Fig. 7/23 illustrates the observed loop densities measured in a Cu 16% Al foil, as a function of irradiation temperature and dose. At low temperatures, the loop density was very high, but as the loops grew very slowly, the irradiation was carried out a high dose before the loops interacted and escaped to the surfaces. As the irradiation temperature was increased, the dose required before slippage became dominant was reduced. At a temperature of 120°C loops were not observed to nucleate after the initial nucleation had occurred. (α) shows the loop density, which included the newly nucleated loops, while β refers to the original loop density. When the rate of decrease of curve β was in excess of the rate of increase of α, or if the new loops stopped nucleating, then the total density of loops quickly reduced to zero and a

dislocation tangle was established with a density dependent on the foil thickness, irradiation temperature and foil stress. It was this form of network, that gave rise to void formation. At high irradiation temperatures, the loops grew so rapidly that the density very soon decreased as a result of loop interaction.

At temperatures higher than 120°C continuous nucleation of small loops was observed during the irradiation and the results indicate that a balance between the rate of re-nucleation and destruction existed which depended directly on the irradiation temperature and dose. Hayns (Harwell report TP590) reached the conclusion that simultaneous nucleation of voids and loops could not occur. Continuous nucleation of loops was observed in Cu 10% Al foils irradiated at 250°C to a dose of ≃70 d.p.a., in very thick foils and voids were not observed, even after this high dose. Thus there may be a link between the early cessation of loop growth and the rapid nucleation of voids, since voids were only observed in Cu 10% Al alloys after an in-situ anneal in the H.V.E.M. prior to irradiation. These foils on irradiation, establish very early in the irradiation, a very stable dislocation network and few loops were observed to nucleate after the initial nucleation at the commencement of irradiation.

7.7 Efficiency of Defect Retention

B.K.M. calculated that the number of vacancies and hence the number of interstitials retained in the foil, either singly, or in loops is given by:-

$$3(t\sqrt{gs\Omega})^{2/3}\ (\frac{g}{\Omega s})^{1/2}$$

Since the total number produced by the irradiation is gt, the efficiency of defect retention is given by

$$\xi = \frac{3(\frac{g}{\Omega s})^{1/6}}{(gt)^{1/3}}$$

Defect retention ratios calculated for pure copper Makin (1968), Nickel and Iron, Bourret (1971), yield values of ξ between .5 and 2.7%. Though the results of Bourret for nickel and iron agreed with his calculated efficiency, there was a discrepancy in Makins results, of a factor of 10. Shimomura (1969) has also calculated the efficiency of retention in electron irradiated gold at 130^{o}K and found a discrepancy in the observed efficiency by a factor of three. Makins results demonstrate the importance of the foil surfaces as sinks for the interstitial atoms, while Shimomura's discrepancies were probably as a result of the experimental difficulty in measuring loop area by electron microscopy. Chen (1971) calculated the retention efficiency in electron irradiated aluminium foils at room temperature and found that the values varied between .014% and .06%, depending on the crystal orientation. This ratio is an order of magnitude less than those observed in copper, nickel and iron and the difference was attributed to the relative mobilities of the interstitials and vacancies produced. In Cu, Ni and Fe, the vacancies are relatively immobile, while in aluminium, both interstitials and vacancies are very mobile, since in this metal, room temperature is well above the stage 3 point defect recovery.

It was suggested, that the mobile vacancies contribute to a higher recombination, effectively reducing the total number of interstitials contributing to loop formation. Theoretical efficiencies calculated using the B.K.M. formula for copper and Cu 16% Al were found to be considerably higher than the experimentally observed efficiencies at several elevated temperatures. However, the experimental results compared favourably with calculations made by Goringe to take into account the effect of diffusion to the surfaces.

The loop density at the foil centre was calculated and the average diameter of the loops measured at various temperatures. Depending on whether the loops were of Frank type as in pure copper or rhombus perfect

as in Cu 16% Al, correction factors were applied to take into account loop projection, in order to measure the average loop area. From this result, the total number of point defects contained in loops was evaluated by multiplying the loop point defect concentration by the measured loop density. Great care was taken in the measurement of loop area and except at the higher temperatures, high resolution weak beam diffraction conditions were used. In pure copper all the loops were of Frank type and measurements were made on loops whose faulted plane was parallel to the foil surface. A projection factor was applied to take into consideration the tilt of 19° from the [111] to the [211] electron beam normal. The results obtained indicate that if care is used quite accurate loop areas can be measured.

In the 'bulk' situation, the efficiency of defect retention follows a $\theta^{-1/3}$ law at large times on the assumption that vacancies are immobile. In the thin foil case, the efficiency for vacancies is increased by retention of those vacancies corresponding to the interstitials migrating to the surface, which in turn decreases the efficiency for interstitials. Graphs of interstitial defect retention efficiency at the centre of the foil as a function of time for several values of P are shown in fig. 7/24. The theoretical calculations carried out by Goringe are shown as solid lines for P values 1, 10, 100 and 1000, while the efficiencies as a function of P are shown as dashed lines. It can be seen that at sufficiently large values of θ, all the curves tend to a $\theta^{-1/3}$ curve, as the increasing density of vacancy defects present take over from the free surfaces as the major sink for interstitials. The experimentally observed retention ratios for copper are shown as triangles, while those for Cu 16% Al are shown as crosses. The measured efficiencies corrected for 'bulk' foils are shown as open circles and squares. Agreement of the corrected bulk efficiencies with the theoretical values were not accurate because the calculations by Goringe for

$\gamma = 1$ were made up to $\theta \simeq 10^4$ and the curve had to be extrapolated to 10^7. However, the defect retention ratios calculated using loop densities measured at the foil centre appear to agree with the calculated efficiencies. The values of retention as calculated by the B.K.M. theory could not account for the observed efficiencies due to the diffusion of mobile interstitials to the surfaces, though when these were taken into account, experimental results agreed to a high degree of accuracy with Goringes computer calculations.

7.8 Loop Size Distributions

In order to correlate the observed defect retention efficiency, with the theoretical values of retention, the variation of average loop diameter as a function of alloy concentration, temperature and dose was measured. Fig. 7/25 illustrates how the loop size distribution varied as a function of dose for a Cu 16% Al foil, irradiated at 240°C. This distribution appeared to be typical of all the Cu/Al alloys during irradiation at elevated temperatures and showed a width at high doses of several hundred angstroms. By contrast however, the loop size distributions predicted by B.K.M. were very narrow and the discrepancy between the two, could not be accounted for by experimental errors.

The calculations of Brown et al (1969) differ from those of Wooley (1963) in that the loops were allowed to have a size distribution, in which a loop of zero radius was taken to be a di-interstitial, which may then grow so that it contributed to the number of loops of larger size at a subsequent time. The basic equation

$$\frac{\partial n}{\partial t} = - \frac{\partial (\dot{r} n)}{\partial r}$$

was used, which reflected, that in time Δt, the number of loops of radius r will be increased by the growth of smaller loops and decreased by the growth of loops in the size range Δr. The B.K.M. formulation assumed that the rate of growth of the loop was proportional to the concentration of the defect of which it was composed and did not depend on loop radius.

The distribution of loop sizes as plotted by B.K.M. showed that the curves have a maximum in frequency distribution N(T) independent of time. The distributions were also skewed slightly towards small loop sizes and had a very narrow 'half frequency width', independent of time. Various possible explanations were suggested to account for the discrepancy between experiment and theory:-

(1) Mobility of interstitials broaden the distribution by random amalgamation.

(2) Loop nuclei being larger clusters of interstitials then two.

(3) Random variation in numbers of interstitial atoms arriving at a given loop.

(4) The number of interstitials which find their way to a large loop is substantially larger than those that find their way to a small loop, because of the larger strain field of the former, thus allowing competitive growth.

The first three of these possibilities were not considered to give rise to any significant increase in loop size distribution, while the fourth possibility has been investigated by Hossain (1974), who considered that a large number of interstitials are generated randomly and join the loop exerting maximum influence, thus causing the loop size distribution to broaden as a function of time. A size distribution was measured for nickel electron irradiated at room temperature, and the number of point defects contained within the loops was calculated. A computer simulation was carried out using the same number of interstitials nucleating as di-interstitials and growing into loops. A circular loop, with Burgers vector normal to the plane of the loop has an interaction between a defect in the loop plane and the loop of

$$U_L = \frac{A}{r}\left(\frac{R}{r}\right)^n \qquad \text{Hesketh (1962)}$$

where R = loop radius

r = distance of defect from loop centre

and n = a function of $^{R}/_{r}$.

The loop exerting the maximum influence, received the interstitial and so a size distribution was established. When comparisons were made, the peak of the theoretical distribution was found to be shifted towards the large loop diameter range, in reasonable agreement with the experimental results. However, no experimental evidence was presented, to account for the significant skew towards the lower size distribution range which was observed to be especially pronounced after irradiation at elevated temperatures.

Chen et al (1973) and Shiraishi (1973) have plotted size distributions in electron irradiated aluminium at room temperature and in Vanadium at 280°C and 460°C. They obtained results similar to those plotted in fig. 7/25, which were measured by considering all the loop diameters within a given area and plotting N(D) as a function of loop diameter directly. The diffraction conditions were g = $[\bar{1}1\bar{1}]$ s > 0 at z = [121] and foil normal F = [111].

The effect of measuring the loop diameter of all loops present in an irradiated area has been compared to the distribution obtained by measuring the diameter of all loops on one plane and multiplying by the number of possible loop planes has been plotted in fig. 7/26. The graph indicates that when all the loops were measured, the number of loops in a given size range N(D) was reduced and the distribution broadened. When loops from one plane only were measured, N(D) increased and the distribution width decreased. The mean diameter of the distribution depended however on the loop chosen for measurement when projection was not taken into account. In general, measurement of loop diameters from a single loop habit plane gave reasonably accurate results but frequently, the loop grew irregularly, so that loop diameter measurements did not reflect the correct loop area. An experimental distribution calculated

by measuring loop area is also shown in 7/26 and can be seen to give a much narrower distribution than diameter measurement of all loops present. Area measurements of loops, to evaluate growth rates (chapter 10) also reveal pecularities of growth not visible when diameter measurements are used. The effect of inside/outside contrast and diffraction vectors on the loop size distribution was investigated, but negligible differences were observed for loops of all sizes.

A further refinement in the technique of measuring loop size distributions, was to image the defects under weak beam conditions, at high magnification. While the technique offers no advantage when measuring large loop diameters, it proved to be useful when measuring size distributions of defects up to 500 Å in size. A foil of Cu 16% Al was irradiated at room temperature for a few minutes, then examined in a 100 keV microscope at high magnification. A diffraction vector g <220> was used to image the defects, with $s \simeq 2 \times 10^{-2}$ Å^{-1} satisfied in dark field. Strong beam conventional images were also taken of the same area and the size distributions obtained were compared in fig. 7/27, in which curve A shows the weak beam distribution. The distribution function N(D) was reduced and was broader in bright field than that measured in weak beam. The whole distribution was also shifted by about 20 Å to a larger size range.

The results obtained, suggest that stringent precautions are necessary when accurate size distributions are to be measured. The loop projection must also be taken into account when meaningful distributions are required. In general, the measurement of distributions from faulted loops presents no problems, since the loop normals are readily obtained. However, when the loops are rhombohedral in shape and have $b = \frac{a}{2}$ <110> (as in the Cu/Al alloys) then great error can occur if the projection is not accounted for.

In order for these correction factors to be applied, measurements were made to define the loop normal, which, in the case of Cu/Al alloys was a few degrees away from the loop Burgers vector. Fig. 7/28 illustates

the distributions obtained for loops grown in a Cu 16% Al foil to different doses. When imaged in diffraction conditions $g = [\bar{1}1\bar{1}]$, $\bar{z} = [121]$ loops with Burgers vectors $b = \frac{a}{2}[1\bar{1}0]$, $\frac{a}{2}[101]$ and $\frac{a}{2}[0\bar{1}1]$ were in contrast. Two of the loop planes, $\bar{n} = (1\bar{1}0)$ and $(0\bar{1}1)$ have been corrected by dividing the loop diameters by .9, while loops on the (101) planes were corrected by division by .6, to reflect the projection. The long loop diameter was measured in all the micrographs, though care was taken in the definition of long diameter, since in many orientations the longer diameter appeared shorter than the 'short' diameter on the prints. When the corrections were applied, the distributions peaked at the same size and the profiles for all measurements were approximately the same. Despite all the precautions fig. 7/28 indicates that the observed distributions were considerably broader than the calculated profiles, even at small loop sizes.

The factors affecting the growth rates of different loops during the same irradiation are of two types:- Those affecting the dissociated ribbon width of the stacking fault and those affecting the point defect concentrations contributing to loop growth. The former include foil stress, loop orientation, loop size and foil temperature. The stress may vary with position of the loop in the foil, though no calculations have been carried out on the magnitude of these stresses. The loop size does affect the dissociation width, but only when they are very small. Since the loops in general grew larger than 500 Å in diameter, the stacking fault width is expected to be similar for all loops in the foil. At high dose rates, the foil temperature may be increased by as much as $50^{\circ}C$ due to direct beam heating, or the presence of the objective aperture, though for dose rates $\triangleq 6 \times 10^{8}$ el/cm^2/sec, the temperature rise was calculated to be $\triangleq 3^{\circ}C$. None of these parameters were large enough to cause the significant differences in observed loop growth rates.

The factors affecting the point defect concentration are depth of

the defect in the foil, position in the beam and the proximity of other loops. Each of these variables have been examined in detail, to find the extent of their influence on growth and they are discussed in chapter 10. Since H.V.E.M. beam profiles are Gaussian in shape near focus, differences in dose rate can occur across the screen, to give rise to different loop growth rates and hence a broad size distribution. However, with suitable choice of bias, condenser 2 and magnification the beam profile can be adjusted to be more or less uniform across the screen, so that the position of a loop in the beam has no observable effect on loop growth rates. The proximity of other loops does influence the loop growth behaviour, though this was observed to be a small modulation on the main parameter, the foil surfaces. However, when the loop density was high, rhombus loops with similar Burgers vectors tended to interact, so that loop agglomeration occurred, with a consequent reduction in loop density and an increase in loop sizes. This effect was often observed in Cu/Al alloys, during irradiation at elevated temperatures.

The diffusion of interstitials and vacancies to the foil surfaces during irradiation produced a variation in point defect concentration with depth in the foil, so that quantitative analysis of the rates of growth of dislocation loops due to clustering of point defects required a knowledge of the distribution of the defects in the foil.

The simultaneous production, recombination and diffusion to the surfaces of vacancies and interstitials during irradiation of thin foils has been considered by Foreman (1972), Goringe (1971), Lam (1974) and Seeger (1975). According to Goringe, a diffusion parameter P was defined to be $as\pi^2/h^2\sqrt{gs\Omega}$, whose magnitude reflected whether bulk or reduced values of interstitial concentrations were produced in the foil. At elevated temperatures, where most of the loop size distributions were measured and in foils $\simeq 2500$ Å, the value of P was high. Under these conditions, the interstitial concentration and the loop concentrations were depressed from their bulk values, as shown in fig. 7/18. When the

value of P was decreased to ≃ 20, after irradiation at room temperature, the interstitial concentration tended towards that of bulk and a more rectangular distribution. Due to the point defect profiles, loops at different depths in the foil grow at different rates.

In order to verify this prediction, a foil of copper was irradiated at 210°C in the H.V.E.M. and the growth rates of Frank loops on planes parallel to the surface (F = [111]) were determined by measurement of the loop areas, to give an effective radius. A layer of gold was then evaporated onto the foil surface, so that stereomeasurements could be made to determine the depth of each defect. The diffraction vector used was g = $[1\bar{1}\bar{1}]$ at z = [211], with a total tilt angle of ≃ 20°. Fig. 7/29 shows the results of growth rates as a function of depth in the foil and the graph indicates that loops at the foil centre, grow at a much faster rate than loops near the foil surface. The diffusion parameter P estimated from loop density measurements to be ≃ 175, did not reflect bulk irradiation conditions. At reduced values of P (low temperature irradiations, thicker foils), the spread in loop growth rates was observed to be substantially reduced. These results indicate, that widely differing growth rates occur as a direct function of the interstitial concentration existing near each loop, at a different depth. Most loops were not parallel to the foil surface, and thus grew into regions of varying point defect concentrations.

Similar results were observed by measuring the long diameter of perfect loops growing in a Cu 16% Al foil during irradiation at 170°C. Only loops with a regular rhombic shape were chosen for measurements. The maximum and minimum growth rates observed were 1.60 Å/sec and .94 Å/sec respectively, with most of the loops growing in the range 1.10 → 1.30 Å/sec. Under these irradiation conditions, after an irradiation time of 1000 seconds, the loop size distribution (depending on the number of loops in each size range) will be at least 200 Å in width.

Since there are two foil surfaces, more loops grow at the slower, rather than the fast rate, with the consequence that the distribution is always skewed. This asymmetry increased with temperature. If the alloy and irradiation conditions were chosen so that continuous nucleation or loop amalgamation did not occur, then the distribution could be completely explained by the foil surface mechanism. The spread in loop growth rates was so large, that any other contributing factors i.e. di-interstitial dissociation Burton (1971) or competitive growth are completely masked.

A plot of a typical size distribution obtained by irradiating a thin foil of Cu 16% Al at 235°C is shown in fig. 7/30. The distribution is split into three sections, A, B and C of which C ($\triangleq$ 10% of the total loop population) represents the very large loops caused by loop amalgamation. Another contributing factor to the asymmetry of distributions at high doses is that dislocation glide can occur, to cause very irregular growth. This can be observed in figs 4/10 and 7/31. Region (B) of the distribution was caused by the effect of foil surfaces on loop growth rates while region (A) was caused by the nucleation of new loops after the initial nucleation period had ended. This effect was commonly observed in Cu 16% Al foils at temperatures in excess of 170°C and contributes as much as 13% to the total loop population. However, at lower temperatures, or in lower alloy concentrations this effect was not observed to contribute to any significant extent to the total loop size distribution.

Fig. 7/32 summarizes the results obtained in a single graph, showing how the various contributions broaden and cause asymmetry in the observed size distributions. The theoretical calculations performed by Brown, Burton or Hayns (1974) have not taken any of these factors into account, with the obvious effect that experimental results bear no resemblance to the predicted distributions.

One interesting observation was the fact that under the same illumination conditions in a tapered foil, the thin areas grew a smaller density of larger loops in the same time. Histograms plotted of the number of loops in a given area as a function of loop diameter and Burgers vectors are shown in fig. 7/34. The diffraction conditions were $g = [\bar{1}1\bar{1}]$, $\bar{z} = [121]$. Curves A, B and C represent three foil thicknesses 4080 Å, 2720 Å and 2040 Å respectively, while loops 1, 2 and 3 represent Burgers vectors $\frac{a}{2}[101]$, $\frac{a}{2}[0\bar{1}1]$ and $\frac{a}{2}[1\bar{1}0]$. When correction factors were applied to the loop diameters, the mean values tended to peak in the same position, in agreement with results plotted in fig. 7/28. It was also evident from the graph, that there was an asymmetry in the numbers of loops on each of the {110} planes. More important however was the fact that at the same irradiation temperature of 215°C and after 300 seconds of irradiation, the thickest foil, represented by curve A ($P \triangleq 36$) produced a narrow distribution of loops with an average corrected diameter of $\triangleq$ 550 Å. As the thickness of the foil was reduced, the function N(D) decreased, with a consequent increase in distribution width and average loop size. The number of Frank loops was also observed to increase as the foil thickness increased. In general, as the value of diffusion parameter P was increased a gradual decrease in N(D) was visible. Thus curve B was representative of a foil with $P \triangleq 60$ while curve C had a P value of $\triangleq$ 110.

This form of size distribution is to be expected, because in the thick foil, a large number of loops compete for interstitials thus giving a slow growth rate. In thin foils a small number of loops compete for interstitials thus giving a fast growth rate, with the consequence that in 4000 Å thick foils, the size distribution will be very narrow.

Fig. 7/33 demonstrates the size increase of the loops, as the foil thickness was reduced. Even though the loops were larger in the thin foil irradiation the total number of point defects stored in the loops

was lower than in the thick foil case indicating that most of the interstitials have been lost to the surfaces. Fig. 7/34 suggests, that if the foil thickness were increased to represent a bulk value (i.e. P = 1), then the size distribution measured would be very narrow in qualitative agreement with the theoretical results.

Experiments have also been performed to show that the foil surfaces only affect the loop size distributions after long periods of irradiation. The loop size distributions have been determined as a function of depth for perfect loops in a Cu 5% Al foil, irradiated at 205°C for a few seconds and a few minutes. Fig. 7/35 illustrates the size distribution obtained as a function of depth when the loops were small. Few loops were observed to nucleate near the foil surfaces, while the highest distribution was obtained at the foil centre. The most interesting observation was however that the distributions had the same mean diameter irrespective of depth in the foil, indicating that the surfaces, while reducing the value of interstitial concentration throughout the foil do not significantly affect the loop growth rates in the very early stage of irradiation.

A second foil of Cu 5% Al was irradiated under identical conditions, but the loops were allowed to grow to significant sizes before the irradiation was stopped, though care was taken to prevent loop interaction. Due to the larger loop sizes, great care was taken in defining the loop depth and measurements were made on opposite sides of the loops in order to define the loop centre accurately. The results of fig. 7/36 indicate that the loop size distributions measured at varying depths in the foil caused a significant variation in average loop diameter, as a direct result of interstitial diffusion to the surfaces. The graph confirms quantitatively that total loop size distributions are considerably broadened, when individual distributions from different foil depths are summated.

However, the diffusion parameter was the same in both experiments, indicating that in quantitative work, the variable θ must also be defined.

A comparison of the total size distributions on the same scale for figs 7/35 and 7/36 is shown in fig. 7/37, in which graph (A), having a width at half height of 95 Å represents the distribution from the foil irradiated for a few seconds. Graph (B) on the other hand has a width of ≙ 900 Å.

Calculations have been carried out by Goringe (unpublished) on the effect that different P values and foil depths have on loop distributions. These results are shown in fig. 7/38 and even though the calculations have not been continued to the long irradiation times experienced in practice, the results indicate that when surface effects are small, fig. (A) the loop size distribution is narrow. In bulk irradiations $P = 10^{-2}$ the distributions from the various depths coincide. The figures 1, 2, 3 and 4 represent the foil centre, 600 Å from foil centre, 1200 Å from foil centre and the mean curve. Graph (4) representing the mean value, has been displaced for clarity. When the surface effects are considerable figs. (B) and (C), the average curve for the whole foil (found as a simple average of curves for several depths) is widened. Even though the loop sizes differ between calculation and experiment by several orders of magnitude, the results are qualitatively in agreement.

7.9 Loop Depth Distributions

Loop depth distributions for a Cu 5% Al foil irradiated at 300°K, 373°K and 473°K, after a few minutes irradiation are illustrated in fig. 7/39. Approximately 200 defects were measured at each temperature, though loops from larger areas had to be measured at 473°K, where the loop density was low. In order to obtain accurate defect depth measurements, the irradiation time at the higher temperatures was reduced to a minimum, so that only small defects were observed. The depth of each

loop from the gold surface layer was measured three times. The results show, that for this alloy, the denuded zone increased in width from about 450 Å to 650 Å, as the temperature was increased.

In order to eliminate image overlap, the thickness of the foil irradiated at 300°K was reduced in comparison to the foil thicknesses used in elevated temperature measurements, but despite the relatively small number of defects measured, the profile of the low temperature irradiated distribution was more rectangular than that of the foil irradiated at 473°K.

There also appeared to be a considerable asymmetry in the loop distribution, especially at elevated temperatures and experiments were performed to test whether this was a 'real' effect, or an error introduced when using the stereoviewer. A specimen of Cu 5% Al was irradiated at 100°C and a layer of gold was evaporated onto the electron entrance specimen surface. An area was marked on the print to enclose ≏ 350 loops and measurements were made using the Hilger-Watts stereoviewer with:-

(1) The prints aligned so that the gold layer appeared nearest the viewer.

(2) The prints reversed to make the gold layer appear away from the viewer.

The results of this experiment are shown in fig. 7/40. Both profiles were similar in appearance, in that more loops were present in the foil near the electron exit surface and confirms that asymmetry in the distributions was not introduced by errors of stereo measurement.

In a second experiment, a foil of Cu 5% Al was irradiated at 210°C and a gold layer deposited on the electron exit surface. Stereo measurements of the distribution revealed that asymmetry was again present but near the top surface of the foil. The distribution suggested that at these temperatures little asymmetry was introduced as a result of non

uniform defect generation throughout the foil. However, by comparing the asymmetry as a function of temperature, it was realised that a uniform profile was being measured at low temperatures, but when the loop densities were low, as in elevated temperature irradiations, the asymmetry began to occur. This was initially attributed to either of two factors:-

(a) A non-uniform distribution of loops as a result of temperature gradients through the foil, caused by the presence of the objective aperture near the electron exit surface of the foil.

(2) The existence of non-parallel foil surfaces. If the foil is wedge shaped, it is immaterial whether the gold is deposited on the upper or lower surface, since loops will be measured in gradually thicker regions as the measured area expands. This effect will tend to give rise to an asymmetry, in which more loops are measured away from the gold surface than near it.

A foil of Cu 5% Al was irradiated at 100°C with and without the objective aperture in position and a gold layer evaporated on the upper specimen surface. Care was taken, to measure loops from a rectangular area of constant thickness as defined by thickness fringes. The results plotted in fig. 7/41 indicate that for the irradiation conditions used, the objective aperture had little effect on the distribution. However, comparison of measurements in a narrow rectangle along a thickness contour, with measurements from a square defining the area, revealed that asymmetry in the profiles was caused by non parallel foils. This asymmetry was thus particularly noticeable at elevated temperatures, since in order to measure a statistically significant number of loops large areas were scanned. All subsequent measurements were made using rectangular areas.

Some of the results of this chapter have been summarized in fig. 7/42. At the foil centre, a high density of faster growing loops are

observed as a result of diffusion of point defects to the surface but the density and growth rates decrease as the distance from the surfaces is reduced. There is also a gradual reduction in loop density, until a point is reached, where no interstitial loops are observed to grow. This has been defined by previous experimenters, as the 'denuded zone', but this is a very nebulous concept since the zone is not well-defined, but exists to a limited extent throughout the specimen thickness. At the electron exit surface, a further denudation may occur at high dose rates and temperatures, if an objective aperture is used during the irradiation. When irradiating under these conditions, the objective aperture should only be inserted a few times, to check for beam or specimen drift, otherwise non-reproducible results may occur.

When all these effects are considered and taken into account, accurate loop density profiles as a function of depth may be obtained.

The experimental depth distributions measured for different P values may be compared with the theoretical profiles fig. 7/18, which were calculated by Goringe (1971). The curves give information on the asymptotic depth distribution of loops, with surface diffusion coefficient P as parameter. It can be seen that the shape of the curve is sensitive to the value of P when the latter is near unity and is relatively insensitive elsewhere. However, the absolute value of loop density at the foil centre, or its average value throughout the foil, is very much affected at large values of P. Fig. 7/43(a) illustrates the depth profiles in a Cu 5% Al foil irradiated at 200°C, having an estimated P value of $\triangleq$ 235, and a loop density at the foil centre of $\triangleq 2 \times 10^{14}$ cm^{-3}. The loop density is very much reduced over the whole foil thickness in comparison to bulk foils and the increase in loop density from the edge of the denuded zone to the foil centre is very gradual. This distribution can be compared to the theoretical profile $P = 10^2$ in fig. 7/23. In contrast, fig. 7/43(b) is a profile, for a foil irradiated at room temperature and

and having P ≃ 35. In this specimen, 340 loops were counted, from a small area in the micrograph. The profile appears to have a much flatter top and the gradient of loop density as a function of depth is much sharper than the case P ≃ 235. In order to compare directly the densities produced by the two irradiations, similar areas must be measured. To take this into account the low temperature distribution or (D) has to be multiplied by ≃ 7.7. This graph thus compares favourably with the profile P = 1 in fig. 7/18. A depth profile was also obtained for a foil having a measured P value of 85, but there was little observable difference between this and the profile for P ≃ 235, fig. 7/43(a).

The growth of vacancy clusters is possible when the rate of arrival per unit volume of vacancies is greater than that of interstitials, the arrival rate being a function of both mobility and concentration. Since irradiation produces the same number of both kinds of point defects and the mobility of interstitials v_i is greater than that of vacancies V_v, nucleation and growth of interstitial clusters takes place after the start of the irradiation unless initially there are sufficient biased sinks to drain the interstitials to concentrations below the threshold for interstitial loop nucleation. The condition $n_v v_v > n_i v_i$ must be satisfied before vacancy loop growth occurs. In electron irradiated thin foils, the surface acts as a biased sink, to reduce the interstitial concentrations to very low values with the consequence that vacancy loops may be expected to nucleate in the regions of the foil denuded of interstitial loops. Fig. 7/44 illustrates a two peaked profile of loop density as a function of depth observed in a Cu 16% Al specimen irradiated at 473°K. The loops imaged near the foil surface were much smaller in size than those measured in the thicker regions. It is possible, that at this temperature the vacancies were mobile enough to agglomerate together in the form of loops, though the exact nature of the small defects has not been ascertained.

A second foil of Cu 16% Al was irradiated at 373°K, but no double peak was observed, indicating that if the loops are of vacancy type, the vacancy is not mobile at this temperature. Observations of stacking fault tetrahedra have also been made in copper, Cu 1% Si and Cu 1% Be irradiated at 473°K in the H.V.E.M. by Ipohorski and Spring (1970), in gold by Rualt et al. (1974) and in copper by Urban and Jager (1975). Small vacancy loops were also observed by Kiritani (Gatlinburg Conf. 1975) in nickel at 75°C and in gold at room temperature.

It appears that impurities act as nucleating agents for vacancy cluster formation. This conclusion is consistent with results from quenching experiments, where impurities have been observed to significantly change the size and distribution of S.F.T. Vacancy loops grow in thin foils due to the preferential loss of interstitials at surfaces. Far away from the surfaces (in thick foils) this effect cannot supply sufficient interstitial denudation and vacancy loops or S.F.T. grow only near dislocations.

The other possible explanation, which cannot be discounted at present, is that oxide or possibly carbonaceous contamination on the foil surfaces can provide impurity ions, which can be implanted into the foil, by transfer of energy from incoming electrons, Rao (1972). These implanted impurity ions can be expected to diffuse in the upper half of the foil, providing nuclei for loop formation and growth. However, in Rao's experiment an electron irradiated aluminium at room temperature, interstitial loops >1000 Å nucleated preferentially near the top surface (i.e. at 1500 Å in a 6000 Å thick foil) but no loops were observed within about 500 Å from the top surface. On the other hand, Fischer et al (1975) concluded on the basis of in-situ annealed thin foil results that impurities (possibly introduced in the electropolish) concentrated beneath the polished surfaces were of no importance in the formation of double peaks in the loop distribution in aluminium. Further, they concluded on the basis of theoretical calculations that

the oxide film which could prevent the point defects from leaving the foil was having an effect only over distances less than 200 Å. They concluded that the observed layer structure in aluminium was due to specific properties of point defects. If the oxide layer or contamination on the surface were giving rise to the double peak, then it would be expected to have occurred in all the other Cu/Al alloys irradiated in the H.V.E.M. However, further experiments need to be performed before a quantitative conclusion can be reached.

7.10 Conclusion

The theories of B.K.M., Bourret and Goringe appear to be able to describe the nucleation characteristics of dislocation loops in copper and copper aluminium alloys when irradiated in the temperature range 273°K to 573°K. The migration energy of a self interstitial atom in copper has been computed to be $E_m = .13 \pm .02$ eV, while a reasonable value of the binding energy between a copper and on aluminium atoms was $E_b \simeq .11 \pm .02$ eV. The chemical reaction rate theory has also been applied to the problem of di-interstitial dissociation and the binding energy of the di-interstitial in copper using corrected loop densities was measured as $E_{ii} = .66 \pm .04$ eV.

Values of defect retention, nucleation time and denuded zones have also been experimentally determined and in general good agreement with theoretical values were obtained, when account was taken of the point defect diffusion to the foil surfaces. The need for a standard irradiation condition has been established which if not adhered to, may yield non-reproducible results. The B.K.M. theory appears incapable of predicting the broad loop size distributions observed in practice at elevated temperatures, which arose mainly as a result of differential loop growth caused by the presence of the foil surfaces. Measurements also indicated that precautions should be taken in order to obtain realistic distributions by including projection factors for each loop

plane. When the loop surfaces are not dominant sinks (thick foils irradiated at low temperatures), competitive growth proposed by B.K.M. and analysed by Hossain can be used to explain the broad distribution.

Depth distributions were also measured as a function of density and defect size and the results are in good agreement with the theoretical predictions.

CHAPTER 8

The Effect of in-situ Anneal Treatments on the Subsequent Radiation Damage in thin Foils

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8.1 Introduction

During a comprehensive study in the H.V.E.M. of electron irradiation damage in copper and copper aluminium alloys over a wide range of elevated temperatures, it was noted that reproducible results concerning defect loop nature, size, density and growth were difficult to achieve. This chapter presents the results of an investigation into how small changes in specimen preparation and annealing procedures may drastically modify the results obtained from different experiments though irradiated under identical conditions. The spread of results noted above, may be explicable in terms of inadvertently imposed differences in pre-irradiation specimen handling.

In chapter 5 of this thesis, it was postulated that hydrogen gas picked up by the specimen during electro-polishing, may be responsible for the variation in results and that prolonged annealing of the foil in the H.V.E.M. at high temperatures after electro-polishing, was required to remove the gas. To investigate this effect in more detail, specimens of Cu N at.% Al (N = 0 → 16) were prepared by electro-polishing in a conventional manner (Nitric acid and methanol) and then annealed in the H.V.E.M. at temperatures T_a for five minutes prior to irradiation by a standard electron flux of 6×10^{18} el/cm^2/sec, at a standard temperature T_i ($T_a > T_i$).

8.2 Preliminary Loop Density Measurements in Cu 16% Al as a Function of T_a

Micrographs of typical results are shown in fig. 8/1 for four values of annealing temperature T_a and an irradiation temperature T_i = 265°C. Two differences were immediately apparent:- the total loop density (even allowing for small differences in specimen thickness) was different for each irradiation as were the proportions of loops which were faulted Frank loops (F) or perfect loops (P). These differences have been quantified in fig. 8/2, where the measured

densities of the two species of loops are plotted against T_a. In this particular experiment, the Cu 16% Al specimen had been annealed at 265°C for 25 minutes prior to the irradiation, with the consequence that most of the hydrogen present in the foil had time to diffuse out. This is reflected in the constant level of measured loop densities up to T_a = 380°C.

As the annealing temperature was increased above ≃ 265°C, a small number of Frank loops nucleated and grew amid the perfect loop network. At annealing temperatures less than T_a = 400°C the majority of defects present in the foil after irradiation at 265°C were rhombus shaped and had Burgers vector $\bar{b} = \frac{a}{2}$ <110>. At an anneal temperature of ≃ 400°C, the measured loop density reached the minimum value, though above this temperature, the total measured loop density increased rapidly to saturate at T_a ≃ 510°C. It should be noticed that the situation of predominantly perfect loops at low T_a was reversed at high T_a, where the majority of loops were faulted Franks. It is likely, that the mean density of perfect loops measured at high T_a is the result of the Frank to perfect loop transformation caused by the nucleation and passage of Shockley partials to clear the stacking fault.

In order to confirm the apparent saturation of density with increasing annealing temperature, one Cu 16% Al specimen was studied in detail at high T_a. The measured Frank loop densities found after irradiation, together with densities 'corrected' for interstitial diffusion to the foil surfaces, have been plotted in fig. 8/3. The corrected densities lie on a surve asymptotic to the corrected density found in a specimen which had been annealed after electropolishing, at 750°C in a high vacuum (10^{-9} torr) furnace for 20 hours before being transferred (in air at room temperature) to the microscope. This curve indicates that for the alloy used, annealing temperatures in excess of ≃ 600°C produce essentially standard specimens, provided that the

annealing takes place after the final thinning.

8.3 Comparison of Loop Densities as a Function of Irradiation Temperature

To investigate the implications of the anneal treatment on the interstitial migration energy E_m and solute binding energy E_b measured from the variation of loop densities as a function of temperature, two specimens of Cu 16% Al were irradiated at decreasing temperatures T_i. The first specimen was annealed prior to irradiation at $T_a = 380^{\circ}C$ while the second was annealed in a U.H.V. furnace at $750^{\circ}C$. The measured loop densities have been plotted in fig. 8.4 and illustrates that numerous sets of loop density results can be obtained from the same foil depending on the anneal temperature T_a.

The high Frank loop densities measured in the $750^{\circ}C$ anneal foil gave rise to significant image overlap, thus causing the measured loop densities to be smaller than they should be. The number of cluster images overlapping will increase with increasing cluster density or foil thickness. However, by considering overlap in successive thin layers of the specimen Chute and Napier (1964) derived a finite series to relate the true loop density to the loop density measured from electron micrographs. Thus

$$\frac{\rho_c}{\rho_T} = 1 - \frac{(x-1)(\sigma n)}{2!} + \frac{(x-1)(x-2)(\sigma n)^2}{3!} + \ldots (-1)^{x-1} \frac{x!}{x.x!} (\sigma n)^{x-1}$$

where $x = t/\bar{d}$

t = foil thickness

$\bar{d}$ = mean diameter of clusters

ρ_c = measured loop density

$\sigma = \pi(\bar{d})^2$

$n = \rho_T \cdot \frac{t}{x}$

Since the measured loop densities in the centre of the foil were in excess of 10^{16} cm^{-3}, a considerable correction was needed. The corrected densities were further adjusted to be representative of bulk foils.

The net result is that the shape of the loop density graph v $\frac{1}{T}$ was increased to give an activation energy $\triangleq$ .22 - .24 eV. Thus the anneal treatment has no effect on the interstitial migration and solute binding energy.

Apart from the change in loop nature and the increase in the loop densities, the curves were of similar appearance in that the gradients were linear at low irradiation temperatures and the di-interstitial appeared to be unstable at high irradiation temperatures.

8.4 Loop Density as a Function of Anneal Temperature for Other Cu/Al Alloys

Investigations were carried out into the extent of the 'annealing effect' in all the Cu/Al alloys, to detect any change in loop density or nature. While no observable increase in loop density was observed, for alloys of concentration less than Cu .31 Al, above this concentration, significant increases in density were observed for the alloys Cu .31, .98, 2, 5, 10 and 16 at.% Al, the actual magnitude dependent on the concentration. Figs. 8/5 and 8/6 illustrate the relative densities of Frank loops and perfect loops as a function of annealing temperature T_a for Cu 2% Al and Cu 5% Al foils. The transition from perfect to Frank loop nature was again quite apparent. In the alloys observed to exhibit the 'anneal effect', perfect loops nucleated below $T_a = 420^{\circ}C$ and Frank loops above this temperature. The actual magnitudes of the loop densities at the transition temperature of $\triangleq 420^{\circ}C$ were subject to considerable error however, due to the small number of loops being measured, though the trend was similar in each experiment. The total loop densities for alloys Cu .98, 2 and 5% Al are plotted in fig. 8/7. It became apparent, that the mean transition temperature from perfect to Frank loop formation was approximately the same for all the alloys, though the range of anneal temperature in which few defects grew decreased, as the solute concentration increased; being $\triangleq 120^{\circ}C$

for Cu .98 Al and ≃ 20°C at Cu 16% Al.

Also included in fig. 8/7 is a single experimental result obtained for a Cu .31 Al foil, after 5 minutes anneal at 550°C. Though this alloy exhibited the 'anneal effect', the saturated loop densities were lower than for the Cu .98% Al alloy. Experiments performed on the Cu, Cu .077 Al and Cu .15 Al, produced no observable change in loop density after several in-situ anneals at 550°C. As in the Cu 16% Al results, a saturation in loop density was observed, the magnitude of which decreased as the solute concentration increased. The temperature at which saturation occurred was also observed to increase as the solute concentration was reduced. This temperature is ≃ 510°C for Cu 16% Al and ≃ 590°C for Cu 2% Al.

8.5 Effect of Annealing Time on the Loop Nature and Density

The loop density as a function of annealing time at a constant temperature T_a = 500°C is shown in fig. 8/8, after each irradiation at T_i = 255°C. The loop density increased very rapidly from ≃ 2 x 10^{15} cm^{-3} to ≃ 1.26 x 10^{16} cm^{-3} in about 5 minutes, though subsequently, little increase in loop density was detected. After about two minutes of anneal, most of the loops nucleated directly as Franks, whereas perfect loops were observed prior to this time.

Fig. 8/9 illustrates the transition which occurs as a function of annealing time for a foil of Cu 16% Al. After twenty minutes anneal at 500°C a large number of very small Frank loops nucleated and grew in conjunction with the larger loops in the foil, causing an asymmetry in the size distribution. As the anneal time was increased to one hour, a significant fraction of the total loop population was of small size. These small loops have been identified as Frank loops, though contrast experiments have not been performed to determine their nature. Unfortunately, stereo measurements were not made on the damage in these foils to ascertain the spatial position of the small loops in relation

to the large loops or the surfaces, and any future experimental work should include such measurements.

One mechanism for the asymmetry in the size distribution may be that proposed by Rao (1972) in which impurities are being bombarded into the specimen to nucleate large loops near the electron entrance surface. This is a distinct possibility in this particular experiment, since quite a significant layer of contamination can build up on the foil surface after 1 hour of anneal in the microscope at 550°C.

A quantitative theory to account for the change in loop nature and density as a result of in-situ annealing cannot be proposed at this time. However, this chapter seeks to propose a few possible explanations for this effect in the light of other experimental data on radiation damage in Cu/Al alloys.

8.6 Effect of Hydrogen Gas on Loop Formation in Cu/Al Alloys

Hydrogen has been shown to promote the nucleation of elongated dipole loops along <112> directions when the hydrogen concentration is low and a high density of rhombus loops randomly dispersed in the foil when the concentration of hydrogen is high, during electron irradiation at elevated temperatures. Mazey (1972) suggested that hydrogen might cause the formation of Frank loops in proton irradiated copper. In order to ascertain whether hydrogen was in some way causing the nucleation of Frank loops after high temperature in-situ anneals, thick specimens of Cu 7% Al were doped using an ion accelerator at Harwell. Specimens were jetted from one side only and then placed in an ion accelerator. The energies of the irradiation were chosen to peak the distribution of hydrogen at 2000, 4000 and 6000 Å from the specimen surface. Lacomit was layered onto the flat surface of the specimen and a final polish at -70°C removed the surface of the dished side only. After the hole had appeared the lacomit was removed by immersion of the specimen in acetone. Careful rinsing of the specimens in distilled water and

ethanol removed any traces of acetone and they were then inserted into the H.V.E.M. for electron irradiation at temperatures between 240°C and 330°C. A very high density of rhombus loops formed, indicating that while hydrogen may promote the enhanced nucleation of perfect loops in foils under these irradiation and microstructural conditions, Frank loops were not stimulated to grow.

Experiments performed in the microscope suggest that hydrogen remains in the Cu/Al foils by a trapping mechanism until the foils are annealed at temperatures in excess of 300°C. The specimens that were hydrogen doped in the Harwell V.E.C., still contained significant amounts of gas, because they were stored at room temperature for only a few hours. The V.E.C. doped Cu 7% Al specimens were also annealed for five minutes at 500°C in the H.V.E.M. and subsequently irradiated at 240°C, but only Frank loops formed.

The possibility also exists, that hydrogen introduced by the polishing treatments could nucleate sub-microscopic gas bubbles which strain the lattice and unfault the Frank loops in the very early stages of growth, though one would expect the same behaviour in pure copper or the very dilute alloys. In-situ annealing of the foils releases the trapped hydrogen and the experimental results are at first sight consistent with the hypothesis that the absence of hydrogen promotes the nucleation of faulted Frank loops. Fig. 8/10(a) illustrates schematically the effect that high temperature annealing has on the distribution of hydrogen gas or sub-microscopic gas bubbles in the foil. When the foil is irradiated without in-situ annealing (point α), stress and hydrogen gas cause the formation of perfect loops to a very high density as a result of the additional nucleation sites. As the foil is annealed, the hydrogen gas is released from the traps, to reduce the nucleation sites and the foil stress. As the anneal temperature is increased further, the foil stress continually reduces,

allowing the growth of Frank loops. Since Frank loops are the most stable defect in low stacking fault energy metals, it is likely that perfect loops are metastable and result only because foil stresses nucleate the Shockley partials to clear the fault.

When thin foils were polished at -70°C (a temperature too low for hydrogen to diffuse into the foil) and irradiated without in-situ annealing, a low density of perfect loops grew (point β), fig. 8/10(a). This result reinforces the conclusion that two processes are operating simultaneously and that while hydrogen may promote the increased nucleation of loops in these Cu/Al foils it is not the prime mechanism for the transition in loop nature and density as a function of annealing temperature. An alternative proposal is outlined in fig. 8/10(c), in which hydrogen gas and 'solute size effect' stress the lattice to promote the nucleation of rhombus perfect, rather than Frank loops.

8.7 Solute Size Effect

Numerous electron microscope studies of secondary defect structures in quenched aluminium based alloys have been reported over the last fifteen years. Three types of defect have been known to form in these alloys given a suitable quenching treatment. They are (i) Frank sessile loops having $b = \frac{a}{3}\langle 111\rangle$ and which may be polygonal or circular in shape, (ii) Hexagonal or circular prismatic loops of Burgers vector $b = \frac{a}{2}\langle 110\rangle$ which form from Frank loops by propagation of a shearing partial dislocation across the fault and (iii) rhombus perfect loops, also of Burgers vector $\frac{a}{2}\langle 110\rangle$ which lie on planes close to $\{110\}$ and characteristically have all four dislocation segments lying on $\{111\}$ planes. In quenched pure aluminium, hexagonal faulted loops were the preponderant secondary defect Edington (1965), Loretto (1966) and only occasionally were rhombus loops observed.

The application of suitable tensile stresses at appropriate times during the quench leads to widespread rhombus loop formation and it

thus appears that the rhombus loop is the lowest energy loop configuration in pure aluminium, though in general its occurrence is prevented by the absence of suitable stresses to initiate the transformation from faulted to perfect. Observations of interstitial loop formation in Cu/Al alloys reveal that if the foil is stressed throughout the irradiation, rhombus shaped loops form, but if Frank loops are allowed to grow and the foil is subsequently stressed (possibly by a contamination layer) then perfect loops occur whose loop normals are parallel to <111>. Further supporting evidence was found in the observations of rhombus loops in neutron irradiated aluminium, Bierlein (1962) and fission fragment irradiated aluminium Westmacott (1962), in which substantial stresses were expected to exist, as a result of irradiation in a reactor environment. It seems that in quenched materials, vacancy condensation in the form of rhombus loops occurs in a suitably stressed lattice.

In attempting to rationalize the secondary defect structures observed in alloy systems, it might be expected that the internal stresses which arise from atomic misfit of the solute additions would fulfil a similar role in unfaulting the Frank loops. Experimental observations from a series of Al alloys by Westmacott (1971) suggest that the concentration dependence of the Frank to rhombus loop transition, varies with alloy concentration. For elements with small atomic misfit e.g. Al/Ag, the transition should occur at high concentrations, whereas for elements with large misfit, there should be a low critical concentration at which unfaulting occurs. In addition, Westmacott found that the stress required to unfault a loop depends on the stacking fault energy γ, which may change with alloy concentration; an increase in γ will tend to increase the unfaulting stress.

A similar behaviour has been found in electron irradiated Cu/Al alloys, the results of which are shown in fig. 8/11. To reduce the adverse effect of dissolved hydrogen, all specimens were annealed in the

microscope for five minutes at 380°C prior to irradiation. The graph illustrates, that the majority of loops in pure copper were of Frank nature, while an increase of aluminium solute produced an increase in the number of rhombus loops. At aluminium concentrations ≥2 at.%, the majority of loops were perfect rhombus with $b = \frac{a}{2} \langle 110 \rangle$.

Attempts were also made, to detect any change in ratio of Frank to perfect loops, as a function of irradiation temperature, but below 150°C, positive identification of the loop nature from H.V.E.M. micrographs became difficult. However, in the temperature range 150°C to 240°C, a very small variation was detected; the lowest irradiation temperature giving the highest number of Frank loops. This result could be interpreted as being caused by Frank loops shearing to perfect loops, as a result of thermal or oxide layer stresses generated at the higher irradiation temperatures. These measurements were made in specimens of thickness ≏ 2500 Å. There is experimental evidence however which suggests that in foils of thickness >3000 Å the ratio of Frank to rhombus loops will increase. This phenomenon needs to be investigated further.

In the analysis, no differentiation was made between rhombus perfect loops on {110} planes or hexagonal perfect loops on {111} planes, but little error results, because only a small number of loops were of hexagonal perfect type. This distinction between the two forms was important, since no evidence has been presented to suggest that irradiation produced Frank loops do actually transform to rhombus loops in Cu/Al alloys. During the irradiations, the transformation regularly observed was the faulted Frank to hexagonal perfect loop on the {111} plane, though these measurements were made on loops which were larger than ≏ 700 Å.

The observations that rhombus loops nucleate and grow in Cu/Al alloys where the stacking fault energy is low is contrary to the

expected formation of Frank loops in such alloys Saada (1962). The stacking fault is removed, if the energy of the perfect loop E_p is less than that of the faulted loop E_f. The relative energies are:-

$$E_f = \frac{2}{3}\frac{1}{1-\nu} Gb^2R\left[\text{ln.}\frac{4R}{r_o} - 2\right] + \pi R^2\gamma$$

$$E_p = \left[\frac{2}{3}\frac{1}{1-\nu} + \frac{1}{3}\frac{2-\nu}{1(1-\nu)}\right] Gb^2R\left[\text{ln.}\frac{4R}{r_o} - 2\right]$$

which gives the stability criterion of Frank loop transformations when

$$\gamma \geq \frac{Gb^2}{3}\left[\frac{2-\nu}{2(1-\nu)}\right]\frac{1}{R}\left[\text{ln.}\frac{4R}{r_o} - 2\right]$$

where G = shear modulus

b = Burgers vector

ν = Poissons ratio

R = Shockley radius

r_o = core radius $\simeq$ 1 Å

According to this criterion, at small sizes, the Frank loop is always stable. Complications occur however with the fact that for interstitial loops, two Shockley partials have to be nucleated as opposed to one for the case of vacancy loops. This must necessarily mean that a higher activation energy barrier must be surmounted before the transformation can occur.

Saada's calculations have been extended to cover the effects of interaction between dislocation loops and impurities or clusters such as G.P. zones, by Veyssiere (1971). A G.P. zone is defined as a region of crystalline irregularity of the matrix resulting from a variation of composition, with the possibility of displacement of the atoms outside the average matrix. The essential characteristic of the G.P. zone

being that is is perfectly coherent with the lattice of the matrix.

The unfaulting of a Frank loop is supposed to occur (following the model proposed by Saada (1963)), when a Shockley loop of Burgers vector b_s and radius r, develops inside the loop F, with Burgers vector b_F and radius R so that $b_F + b_S = b_P$ (the Burgers vector of the perfect dislocation.) Writing

$$\gamma_c = \frac{\mu b_s^2}{4\pi K b_o}$$

where μ = shear modulus

K = constant, between $1-\nu$ and ν

b_o = core radius,

Saada found that if $\gamma \geq \gamma_c$, the Shockley loop grew spontaneously. If $\gamma < \gamma_c$, the Shockley loop growth (inside the Frank loop) depended on the value of activation energy $W_s(r_c)$, so that faulted or unfaulted loops may be observed simultaneously.

In the case of pure metals, this formulation describes the nature of the loops, but for solid solutions, other factors must be taken into account. If a shear stress is applied on the Shockley loop plane by a spherical G.P. zone for example, the expression for the Shockley loop energy is:-

$$W(r) = W_s(r) + W_{int}(r)$$

where

$$W_s(r) = W_o \left(\frac{2r}{b_o} \log \frac{r}{b_o} - \frac{r^2}{b_o^2} \frac{\gamma}{\gamma_c} + \frac{\gamma}{\gamma_c}\right)$$

is the Shockley loop energy and $W_o = \pi b_o^2 \gamma_c$

γ = measured stacking fault energy.

$W_{int}(r) = \int_s b_s \Sigma \, dS$ and is the interaction energy between the zone and the loop. The tensor Σ represents the stresses generated by the zone while s is the loop surface. Veyssiere (1971) computed the interaction energy and found that the size effect due to a single atom of Al

in a copper matrix was not great enough to reduce sufficiently the activation energy $W(r_c)$, in order to influence loop formation. However, when clusters of atoms occur, as in G.P. zones, the activation energy $W(r_c)$ can be considerably reduced, so that Frank loop unfaulting can occur. Veyssiere carried out calculations for Al-Zn and Al-Ag alloys, where precipitation of spherical G.P. zones occur.

The main conclusion that impurities or clusters consisting of a few atoms cannot stress the lattice significantly to permit the Shockley partial to reach its critical radius invalidates Westmacott's conclusion that misfit stresses alone can cause the Frank to perfect loop transition. It is quite likely, that his quenching treatment allowed the formation of small clusters, which could then cause the Frank loops to disappear. For the Al-Zn system, analysed by Veyssiere, the activation energy to nucleate the Shockley in the absence of clusters was about 8 eV. However, when the radius of the inclusion was $\simeq$ 30 Å, at a distance of 30 Å from the Frank loop, the activation energy was reduced to less than 1 eV.

Thus it seems, that in fig. 8/10(c), the solute size effect cannot explain the loop nature at the low annealing temperatures. The possibility that aluminium could be diffusing to the specimen surface to leave a copper rich region in the foil centre has been considered, since it is known that Frank loops preferentially form in copper rich alloys. However, this solution has been rejected for the following reasons:-

(1) There is no real driving force for a mass diffusion of aluminium to the surface.

(2) It is unlikely that in foils of Cu 16% Al enough solute could be diffused, to completely denude the foil centre of aluminium, so that Frank loops were nucleating in regions <2 at.% concentration.

(3) A high density of perfect loops would nucleate at each foil surface, since the solute concentration would be very high.

These effects have not been observed.

Thus the thin film which accumulates on the specimen surface after high temperature anneals was not due to diffusion of aluminium to the foil surfaces, but was probably an oxide layer which has not been presumed to affect the loop nature or density to any significant extent.

8.8 Short Range Order in Cu/Al Alloys

Although it is well known that copper rich Cu/Al solid solution alloys containing up to 20 at.% Al exhibit short-range order, Houska (1959), Kagan (1961), Cahn (1962), Borie (1964), Kastnel'san (1966), Gaudig (1969), there is yet no agreement on how to characterize the local atomic arrangements in these alloys. An investigation by Gaudig et al. (1969) involved electron diffraction, electron microscopy and electrical resistivity measurements in alloys containing from 10 → 20 at.% Al. The authors claimed to have demonstrated that the short range ordered state consists of a stable fine dispersion of regions of long range order in a disordered solid solution matrix and that a stable superlattice phase forms at an aluminium concentration greater than 20 at.%. Borie and Sparks (1964) in their investigations of the short range order in single crystals of Cu 16% Al presented the scattering distribution in a few planes of the reciprocal lattice, in which the intensity was concentrated in diffuse satellite peaks arranged in a four fold symmetrical pattern about the normal F.C.C. superlattice positions.

The actual equilibrium state seems in doubt and two explanations have been proposed:-

(1) The copper aluminium solid solution α phase is attempting to order into a definite long range ordered structure but fails to attain equilibrium order solely for kinetic reasons.

(2) The α phase is only in a short range ordered state.

Gaudig argues in favour of the first interpretation with the proviso that the alloys may be in an equilibrium state even though such a state

clearly does not represent long range order. Borie et al. (1964) however, favour the second explanation and they proposed a tetrahedral configuration of aluminium atoms which form second neighbours along the short edges of the tetrahedra but have a maximum number of copper atoms as first neighbours. Gehlen and Cohen (1965) have performed computer calculations of the atomic arrangements in Cu 16% Al alloys, using the Houska-Averbach short range order coefficients as input parameters. The computer generated structure did not reveal isolated tetrahedra but contained irregularly shaped clusters of aluminium atoms joined as second-neighbour pairs. Most of the clusters or domains of order in the simulation of Gehlen assumed a rod shaped configuration not unlike the sequence of tetrahedra mentioned above.

Measurements of specific heat of Cu/Al alloys by Matsuo (1963) suggest a critical temperature for ordering at about 300°C. Also, as local order develops, the asymmetric size effect scattering is enhanced and this may be associated with the strain contrast observed by Gaudig (1969) using electron microscopy, due to the probable increase in the strain field with increasing short range order. Thus the short range ordering effect can be related qualitatively to the nature and density of radiation damage loops formed in the H.V.E.M. When copper aluminium alloys were annealed at temperatures $T_a > 400^{\circ}C$ and effectively quenched to the irradiation temperature of $T_i \triangleq 240^{\circ}C$ the total loop density and density of Frank loops increased. This was probably due to a disordering of the copper aluminium lattice and a corresponding reduction of strain energy associated with the ordered Cu/Al domains. Quite clearly, if the lattice stress were being relieved, the Shockley partials could not nucleate in the Frank loops, so that an increasing number of Frank loops would be retained as T_a were increased. The absence of stress would also lead to a higher number of loops being nucleated and a saturation of total loop density when the foil became stress free.

Below the critical temperature for ordering, small domains of ordered structure appear, surrounded by a disordered matrix. These domains can be considered analogous to the G.P. zones discussed by Veyssiere (1971) for Al-Zn alloys, in that they can stress the lattice sufficiently to promote the formation of rhombus loops. Measurements of the loop types formed in different Cu/Al alloys Fig. 8/11, suggests that below Cu 2% Al, the domains of order must be very small and strain the lattice very little, to allow the simultaneous production of Frank loops and rhombus loops. The proposal that short range ordering mechanisms strain the lattice is also consistent with the fact that when specimens were polished at $-75^{o}C$, a very low density of rhombus loops formed on irradiation.

8.9 Ordered alloys as Hydrogen Traps

Several ordered compounds Mg_2Cu and Mg_2Ni Reilly (1968), Ti_3Sn Jones (1972), Co_5Re and Ni_5Re Zylstra (1969) have been found to absorb hydrogen which is randomly distributed in all equivalent interstitial sites at high temperatures but is distributed in an ordered array on those same sites at low temperatures. Because they absorb very large quantities of hydrogen at room temperature or below such compounds have been suggested as a kind of solid state 'fuel tank' for hydrogen based transportation systems. Gol'tsov (1971) also found that the coefficients of hydrogen diffusion and permeation are affected by the state of order in alloys, such as Cu_3Au, Ni_3Fe, Ni_3Mn, Cu_3Pd and Ag_2Pd_3. Further effects of hydrogen ordering have been observed in niobium foils on the {100} and {210} planes after electrolytic charging by Schober (1975), and in nickel electro-deposit Nakahara (1976) where hydrogen gas bubbles incorporated preferentially along <001> to form linear defects similar in appearance to those formed in Cu/Al alloys.

The possibility of ordering in austenitic alloys Fe/20Cr/55Ni and Fe/20Cr/40Ni has also been suggested by Thomas (1963). This may be

an important parameter in the nucleation of loops and voids in these alloys, though no work has been published on the effect that ordered alloys may have on the nucleation of these defects.

The short range order hypothesis is also consistent with the observation, that vacuum annealed bulk slices at 750°C on irradiation produced only perfect loops, but thin foils annealed in the U.H.V. furnace at the same temperature formed Frank loops. The order-disorder phenomenon in Cu/Al alloys is closely linked to the specimen heat treatment. According to Scattergood (1970) furnace cooled bulk specimens which were prepared by annealing under vacuum at 650°C for 24 hours and cooled to room temperature at 5°C/hr. produced a large degree of short range order, while quenched specimens developed a very low degree of order. These results are consistent with the in-situ anneal treatment given to the specimens in the H.V.E.M. because the cooling to the irradiation temperature T_i takes place very rapidly and can be considered as quenching, because the foil thickness was <3000 Å. Since the copper aluminium foils are ordered, hydrogen from the electropolish bath can diffuse in rapidly and form precipitates in well defined directions, depending on the amount of hydrogen.

The most informative diffuse X-ray scattering measurements are those of Borie on a single crystal containing Cu 16 at.% Al. It was concluded from the results that the aluminium atoms in the alloy were distributed on the atomic sites in the face centred cubic structure in groups of four so that they form a tetrahedral array in the manner illustrated in fig. 8/12(a) and (b), all other sites in the two unit cells of the f.c.c. structure being occupied by copper atoms. The tetrahedron of aluminium atoms are not regular as the edges of the tetrahedra are not equal and in the configuration of 8/12(a) the elongation of the tetrahedron is parallel to the Z axis. There are six possible orientations for the tetrahedra of aluminium atoms and the

two shown in fig. 8/12 are related by a rotation of 90° about the z axis. All orientations of tetrahedra are equally probable and the restriction on their arrangement, from the results of Borie is that no two tetrahedra can be so close as to result in Al-Al nearest neighbours. The arrangement of copper and aluminium atoms in neighbouring {111} planes which results from tetrahedral packing is illustrated in fig. 8/12(c). When interstitial hydrogen is present in the Cu/Al foils after electrolytic polishing, possible directions for accommodation could be along the <112> directions, as shown.

8.10 Domain Structure

Gaudig (1969) reported electron microscope observations of short range order in a number of alloys, including Cu 16% Al. The foils exhibited a freely dispersed contrast effect, which was interpreted in terms of a profusion of weak localized strain fields, which developed to the so called 'tweed pattern', characteristic of alloys containing coherent precipitates. In cases where single 'black-white' images typical of small strain centres were observed, the intensity distribution was not unique and a simple function of operative diffraction vector $\bar{g}$, indicating that neither a direction of maximum displacement nor a unique shape effect were common to all groups of the strain centres visible. Gaudig Z. metal. (1969) using the width of X-ray reflections for Cu/Al alloys calculated an approximate diameter of the ordered region of about 20 Å, while resistivity measurements gave a diameter of between 10 and 20 Å. The density of domains was estimated to be about 6×10^{18} cm^{-3}.

A similar background speckled structure was imaged in a Cu 16% Al specimen as shown in fig. 8/13. The diffraction conditions were $\bar{z}$ = <211>, g = <111> weak beam with $s = 2 \times 10^{-2}$ $Å^{-1}$ satisfied. The foil was electropolished at -40°C and 4.4 volts then imaged in a 100 keV microscope. The diameter of the white contrast regions and the density are consistent with those suggested by Gaudig. This particular

specimen was known to be ordered, because the bulk slice had been annealed at 1000°C for some hours, then very slowly cooled to room temperature. After subsequent transferal to the H.V.E.M. irradiation at ≏ 200°C produced only rhombus perfect loops consistent with the fact that the small domains were indeed straining the lattice.

8.11 The Nature of Small Defect Clusters in Cu/Al Alloys

The observation that rhombus loops grow in Cu/Al foils without an in-situ anneal raised the question as to whether these loops nucleated as such, or as Frank loops, which then suffered a shearing transformation when the loops were submicroscopic in size. A theory for the formation of rhombus loops from Frank loops has already been presented in this thesis, in which, by a process of glide and climb, the Frank loops can shear and then rotate to the minimum energy habit plane of the rhombus near the {320} plane. Unfortunately, this transition has not been observed in the H.V.E.M. Instead, when the Frank loops unfault, either as a result of contamination or loop interaction, a perfect hexagonal loop of Burgers vector $b = \frac{a}{2}\langle 110\rangle$ results, with a foil normal between <111> and <110>.

These observations were made when the Frank loops were >1000 Å in diameter so it is likely that (1) loop size, (2) dissociation width (3) contamination stress, (4) solute impedance, determine the final orientation. A further experimental observation showed that while small glissile loops formed in alloys of concentration > 2% Al had an exact rhombus shape and lay near {320} planes, glissile loops in the dilute alloys < 2% Al had very curved sides when imaged under the same conditions. Preliminary experiments revealed that these loops had habit planes between {111} and {110}.

Loops of ≏ 120 Å in diameter formed at room temperature in a Cu 16% Al foil were imaged in weak beam and found to be of perfect nature. However, for loops of a size too small to be determined even by the

weak beam technique the loop nature was determined using the black-white contrast technique. Reviews of this analysis have been given by Ruhle (1969) and by Wilkens (1970). Under dynamical two beam conditions, small strain centres located sufficiently close to either one of the foil surfaces (within about 1 - 1.5 ξ_g) produces a characteristic black white contrast figure which in general consists of one black and one white lobe. The orientation of a B.W. figure is characterized by the so-called black white vector $\bar{l}$, which points from the centre of the black lobe to the centre of the white lobe. Recently, the properties of such figures have been extensively studied both by experiment and by contrast calculations. As a result, it was found that the properties of the contrast depend in a characteristic way on the type of strain centre and its orientation or position in the foil.

Determination of the direction of the Burgers vector $\bar{b}$ of small dislocation loops has been carried out by Ruhle (1965), (1967), McIntyre (1967), Yoffe (1970) and the general conclusion for Frank loops is that the direction of $\bar{l}$ corresponds within a few degrees to the projection of $\bar{b}$ onto the image plane. This property can conveniently be used in the identification of Frank loops, where the Burgers vector $b = \frac{a}{3}\langle 111\rangle$ is perpendicular to the loop. In this particular case, the analysis is facilitated by the fact that the number of possible Frank loop configurations in foils is restricted by crystallography to four. The original calculations were computed for Frank loops whose loop habit plane was confined to the image plane. However, at the [110] orientation from the point of view of an incident electron beam, there are two {111} planes which are inclined to the direction of the beam also capable of producing black white images, though with less contrast. Computations by Saldin (1975) using the conditions of strongly excited reflections (111), (002) and (220) revealed, that in all cases, the $\bar{l}$ vectors were nearly parallel to $\bar{g}$. When $\bar{g}.\bar{b} = 0$, the loop is viewed by the so called residual contrast. Only the components of the displacement field in a

direction perpendicular to $\bar{b}$ contribute to the contrast. Since these components are weak compared to the components parallel to $\bar{b}$, the images are considerably weaker than those for which $\bar{g}.\bar{b} \neq 0$. If $\bar{b}$ and $\bar{n}$ are close to, but not both within the plane perpendicular to $\bar{g}$, the black and white lobes can be strongly distorted, leading to a splitting of the two lobes into main lobes and subsidiary lobes. Since this complicates the identification of perfect loops, a search was made in electron irradiated Cu/Al foils only for Frank loops. Thus loops which were not characterized as Franks were assumed to be perfect.

Since a large zone denuded of loops exists at each specimen surface, loops could only be formed in the thicker areas of the foil. Thus only a small percentage of loops gave rise to the characteristic black white contrast. The defects were imaged at a magnification of 66,000 times in the diffraction vectors g = <111> and <200>at the three <110> beam directions. The micrographs were then enlarged to $\simeq$ 225,000 times in order to detect as accurately as possible the vector $\bar{l}$. Due to the depth of the defects, the g <220> diffraction vector produced no visible black white contrast.

Under dynamical image conditions, the lateral extension of the contrast figures for a defect cluster of a given size is rather sensitive to the actual diffraction conditions and especially to the depth and position of the cluster in the foil. Measurements of loop diameter were thus made under kinematical conditions, since the widths of the black dot contrast figures are much less sensitive to the actual image conditions.

Of the several hundred loops in the micrographs, only 103 could be identified as having a measurable B.W. contrast direction. Seventy of these loops were identified as perfect and thirty three as Frank loops. The relative size distributions of the two types of loops are shown in fig. 8/14, which indicates that if Frank loops nucleate, the transition to rhombus perfect shape must take place at a very early stage in its

history. One possible explanation for the regular rhombus shape is that when the transformation occurred the loops were undissociated and so allowed the rapid climb and glide of the dislocation segments to ≃ {012}.

The experimental investigation into the nature of small loops was inconclusive, due to the mixture of Frank and perfect loops observed, but not inconsistent with the hypothesis that rhombus loops nucleate as Franks, but transform at very small sizes. The results also show an overlap of loop diameter for both types of loops and it seems possible that while some loops may nucleate as Franks others may probably nucleate directly on the {110} planes.

The different shape of the perfect loops in the dilute alloys is also not inconsistent with the proposal that these loops nucleate as Franks and transform subsequently to perfect shape, while the large majority of rhombus loops formed in Cu 16% Al nucleate directly on {110}. Further evidence lies in the fact that dipole loops formed in the high concentration alloys during the early part of the irradiation could not possibly be nucleated on {111} planes, due to the nature of the Burgers vector and the loop line direction. It is also of interest to note that these dipole loops do not appear in the very dilute alloys, where the loops are normally expected to nucleate as Franks.

The activation energy to nucleate a Shockley partial inside a Frank loop, using the formula developed by Saada (1962) was calculated for three metals, copper, Cu 5% Al and Cu 16% Al. It was immediately apparent that in disordered foils of any alloy concentration the Frank loop is going to be the stable defect, since the activation energy to nucleate the Shockley partial is very high. The dissociation of the Frank partial into a Shockley and a stair-rod dislocation will tend to increase the stability even further, thus the Frank loops observed in the H.V.E.M. after irradiation in general grew to much larger sizes in the alloys compared to pure copper.

8.12 Conclusion

Thin foils of concentration in excess of Cu .31 at.% Al when annealed in the microscope prior to irradiation were found to nucleate an increasing number of Frank loops, depending on the temperature of the anneal. This behaviour compared to the low density of perfect loops nucleated in foils which had not been given an anneal treatment. Bulk foils of the same alloys however reacted differently, when subjected to the same treatment, in that rhombus loops always nucleated on irradiation, irrespective of the temperature of the bulk foil anneal. The annealing temperature at which rhombus loops ceased to nucleate and Frank loops grew was found to be constant at $\simeq 420^{\circ}C$ and that the loop density saturated at temperatures between 500 and $600^{\circ}C$.

The results of the experimental work suggested that no single factor was causing the loop nature and density to change as a result of anneal temperature. It was concluded however that the presence of electropolish induced interstitial hydrogen gas was promoting the dramatic increase in loop density in foils annealed at temperatures up to $400^{\circ}C$, but that the presence of short range order possibly in conjunction with other gases in the Cu/Al foils, was responsible for the nucleation of perfect loops. Annealing of the thin foils at elevated temperatures was assumed to relieve the foil stress by destroying the short range domain structure. However, in the absence of further experimental evidence, these conclusions can only be regarded as tentative.

Further work needs to be carried out into the detailed effects of S.R.O., hydrogen gas and crystal perfection on the loop formation in other alloys especially those steels having commercial significance.

CHAPTER 9

Void Growth in Copper Aluminium Alloys

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9.1 Introduction

Many techniques have been used for introducing defects into metals and one of the most informative has been that of electron irradiation. Since reactor irradiation damage effects are complex, there appear to be considerable advantages in the relatively simple character of electron damage. There is a continuous production of single point defect pairs, in a well controlled manner, uncomplicated by transmutation effects, the introduction of impurities or of cascades. Electron irradiation is thus particularly appropriate for investigating single point defect behaviour and the void phenomenum lies in this category, though it differs from previous electron damage studies reported in this thesis, in that very high irradiation doses are required. A natural consequence of the very high doses (expressed in displacements per atom) is that several months reactor damage can be simulated in a few hours in the H.V.E.M. and that individual void growth can be followed.

Even more stringent precautions are required to obtain consistent void swelling results than were needed to promote the nucleation and growth of dislocation loops, since the dose rates and irradiation temperatures are much higher. In the void experiments described in this thesis, particular attention was paid to the following:-

(1) Foil thicknesses chosen to be representative of bulk specimens.

(2) Inhomogeneity in the electron beam.

(3) Inadvertent specimen temperature rises due to badly clamped specimens or heating from the objective aperture.

(4) Ion damage in the foil. This was prevented by conditioning of the H.V.E.M. after about 1½ hours of irradiation.

The first observation of void growth occurred during the examination by electron microscopy of stainless steel fuel cladding, that had been irradiated in the Dounreay Fast Reactor by Cawthorne and Fulton (1967). The void observations implied dimensional changes that would constitute

a serious technological problem in commercial scale fast reactors. Radiation induced voids have therefore been the subject of investigation in many different pure metals and alloys, using several irradiation techniques, the results of which have been published in the following conference proceedings:-

Radiation Damage in Reactor Materials I.A.E.A. Vienna (1969).

B.N.E.S. Conference Loading (1971).

Radiation Induced Voids in Metals A.E.C. Symposium 26 (1972).

Physical Metallurgy of Reactor Fuel Elements Berkeley (1973).

Irradiation Behaviour, Fuel Cladding and Core Components Karlsruhe (1974).

Irradiation produced voids A.E.R.E. 7934 (1975).

The void results obtained prior to 1971 have been reviewed by Norris (1972), while a more theoretical review has been presented by Bullough and Nelson (1972). Since the pioneering work by Norris (1971) and Makin (1971) using the H.V.E.M. to simulate void formation, interest in the study of void swelling using this technique has grown rapidly. In fact, so many results have been obtained using electrons, ions and neutrons that it would be a difficult task to list every observation. Instead, only a few results have been included, which are considered directly relevant to the nucleation or suppression of void growth in Cu/Al alloys.

9.2 The Effects of Minor Element Additions on Void Growth

The sensitivity of swelling in pure metals to impurities and minor element additions was recognized in the early investigations of void swelling. Steigler et al. (1969) described the greater resistance to swelling of neutron irradiated commercial aluminium as compared to high purity aluminium; and Holmes (1969) reported similar suppression by impurities in Ni. Other investigations of swelling inhibition by very small amounts of impurities have been carried out in Al and Mg Adda (1972)

and Jostons et al (1971), Ni Adda (1972) and Brimhall (1972) and V by Wiffen (1972) and Santhanam (1973). The effect of only 100 ppm impurity in neutron irradiated Mg was particularly striking. Suppression of swelling by deliberate single element additions have been reported also in a variety of metals including Al containing V, Cu, Fe, Risbet (1975), In, Si Mayer (1974), Copper containing Be Makin (1971) and Ni Brimhall (1972).

The amount of swelling suppression is specific to the minor element that is added. For example the work of Silvestre et al (1974) and Smidt et al (1974) indicated that 1 at.% Fe had little effect on the swelling of Ni; 1 at.% Al caused some swelling reduction; 1 at.% Si had a large effect and 1 at.% T_i or Mo provided almost complete suppression of swelling. Some minor element additions appear to cause an increase in swelling, examples of such behaviour being Ag or Mg in Al Risbet (1975); Al Wolfenden (1972) or Cd Makin (1971) in Cu and T_i in Mo Moteff (1975). Levy (1975) reported the work of Risbet, in which Ag and Mg increased the swelling of Al, while V, Cu and Fe decreased it. Makin (1971) also demonstrated a large increase in swelling due to the addition of 1 at.% Ag to Cu.

Although the details of swelling suppression vary from system to system, in many cases the swelling of a pure material can be reduced by a factor of ten by the addition of the order of 1% of selected elements. Characteristically the minor additions tend to increase the incubation dose rather than change the subsequent swelling rate. As a result, the swelling inhibition at low dose does not provide a reliable indication of the benefit that alloying will provide at high damage levels. However, the interest in irradiating pure metals containing single alloy elements is not in directly developing a low swelling alloy, but rather in characterizing the behaviour of a simple system with the expectation that an understanding of simple alloys will lead to an understanding of

the more complex commercial alloys.

9.3 Discussion of the Experimental Results Obtained from Copper Aluminium Alloys

The aim of the work performed for this chapter was not to quantitatively analyse the void swelling in Cu/Al alloys, but to relate the microstructure of loop damage to the onset of void nucleation. Levy et al. (1971) in their study of Cu 7 at.% Al expected to favour the formation of faulted loops, by lowering the stacking fault energy of copper. However, they observed no evidence of any kind of radiation damage using a neutron dose of $\triangleq 5 \times 10^{20}$ n.cm^{-2}, E > .1 MeV, $T_i = 250^{\circ}C$ and suggested that the extended dislocations might be equally effective as sinks for radiation produced vacancies as for interstitials, or that all the vacancies may have been recombined with the interstitials. Wolfenden (1972) irradiated a Cu 10 wt.% Al specimen to a fluence of 1.3×10^{22} neutrons/cm^2 at a calculated temperature of $175 \pm 25^{\circ}C$. Equiaxed and elongated voids were seen, whose distribution was non-uniform, the voids often being associated with particles and dislocation tangles. The void density was estimated to be about 10^{11}/cm^3, and had sizes 3500 Å (equiaxed) or about 4500 Å (elongated). Arrays of tangled dislocations and small dislocation loops were also observed in the irradiated alloy. Cu 10 wt.% Al is not a single phase alloy however and Wolfenden recorded that small γ_2 precipitates were associated with the voids. Levy's interpretation of the absence of radiation damage, that extended dislocations are effective sinks for both vacancies and interstitials is clearly at variance with the observation that dissociated loops climb during irradiation.

Fig. 9/1 shows the void densities in some Cu/Al foils irradiated at $250^{\circ}C$ to a dose of 45 d.p.a. at a fluence of 4.5×10^{-3} d.p.a.sec^{-1}. The onset of void growth was observed at about 5 d.p.a. for copper and Cu .31 Al and at $\triangleq$ 15 d.p.a. for the Cu 2% Al alloy. Voids were not

visible in the Cu 5% Al and Cu 16% Al alloys irradiated to doses of 50 and 67 d.p.a. respectively. Fig. 9/1(d) indicates that a foil of Cu 10% Al irradiated to 45 d.p.a. generated only a dense dislocation tangle and a high density of small black dot images. At this stage, it is too early to say that void swelling is suppressed in the high concentration alloys, since it is possible that some void growth may take place after irradiation to high doses. However, it is clear that the incubation period before which voids appear, was substantially increased as the alloy concentration was increased.

There also appeared to be a relationship between the loop nature and the subsequent void formation as can be seen from fig. 8/11, which shows the ratio of Frank loops to total loop population as a function of increased alloy concentration. In alloys of concentration up to and including Cu 2% Al, a considerable number of Frank loops were present, after the initial irradiation, possibly corresponding to the ease with which voids were nucleated in the dilute Cu/Al alloys. In the alloys of concentration > 2at.% Al, only rhombus perfect loops were observed to nucleate and grow, corresponding to the absence of voids in these alloys. It was very difficult to correlate the loop nature with void growth and swelling in most of the published work, since no data on the initial dislocation network was generally given. There appears to be a serious gap in knowledge of the relationship between loop nature, loop density and dislocation density and the subsequent void nucleation characteristics.

However, radiation damage in F.C.C. pure metals in general produced Frank loop growth as can be seen from the reported results in Cu, Ni, Al, Ag etc. Frank loop growth has also been reported in various irradiated steels Mazey (1972) and in these alloys, high void swellings have been observed. Fe/Cr/Ni alloys have also been shown to give high volume swellings Harries (1974) and specimens of Fe-15Ni-16Cr with < .005C, irradiated at 450^{o}C formed very irregular Frank loops. Makin (1971)

reported that void growth was inhibited up to 100 d.p.a. in a Cu 1.2% Be foil irradiated at 250°C. Analysis of the results of Ipohorski and Spring (1971) for electron irradiation in Cu/Be alloys, revealed that a large number of rhombus perfect loops were present. Mazey and Menzinger (1973) reported that neutron irradiated Cu/Ni alloys of high concentration resulted in no void growth. In alloys, where zero or low void growth rates were reported, a low density of 'black spot defect' clusters and a high density of prismatic dislocation loops formed; the latter increasing with respect to the former as the nickel content was raised. Since the Frank loops eventually shear to form perfect loops and subsequently a dense tangle of $b = \frac{a}{2}$ <110> dislocations, similar to the network arising from the interaction of rhombus perfect loops, it appears that factors controlling the nucleation of such loops also controls the subsequent void formation.

9.4 The Mechanism of Void Nucleation and Growth

During irradiation in the H.V.E.M. foil surfaces can influence the interstitial and vacancy concentrations to form denuded areas, where vacancy supersaturation is low and void growth restricted. This effect has been considered in detail by Garner and Thomas (1972). The second restriction on void swelling is that under the influence of image forces Makin (1972), dislocation loops generated by irradiation can unfault and slip to the foil surfaces, Norris (1970). Thus below a critical thickness, the foil may be unable to maintain a sufficiently high dislocation density to provide biasing for rapid void formation and this can become serious in pure metals. The influence of dislocations on the nucleation of voids in nickel has been studied by Harbottle (1973). The minimum foil thickness for nickel electron irradiated at 400°C was found to be 4000 Å and voids were found not to nucleate if the dislocation density was less than 10^9 lines/cm^2. Harbottle also found that voids were observed when the dislocation density reached its maximum and that the

higher the density, the lower was the dose required to observe the voids.

Foil thicknesses > 5000 Å were used for the irradiation of Cu/Al alloys to nucleate voids, so that the evolved dislocation densities were not influenced to a significant extent by the proximity of the foil surfaces. In alloys Cu 5, 10, 16% Al, voids were not nucleated at doses of 67 d.p.a., even though various temperatures between 175°C and 320°C were used for the irradiation, to take into account the suggestion by Adda (1971) that for Cu/Al alloys, the vacancy mobility is increased, so shifting void formation to lower temperatures. However, Li and Nowick (1956) using a stress relaxation method have measured the vacancy mobility in a Cu 15% Al to be ≃ 1.08 eV, with the possible consequence that maximum void swelling in the Cu/Al alloys will tend to occur at higher temperatures than that for maximum swelling in pure copper. However, even at 320°C, where the vacancy is mobile, no voids were observed.

The effect of dislocations on the kinetics of void formation can be discussed in terms of the degree of biasing of the point defect concentrations. The rate of arrival of excess vacancies at voids is determined by the bias factor and the total sink annihilation probability. The bias factor represents the degree of preference of interstitials to dislocations and should remain constant as a function of dislocation density as long as climb is not impeded. However, the total annihilation probability increases in direct proportion to the dislocation density, which means that around each dislocation, there is a cylinder in which the dislocation affects the relative defect concentrations by preferential absorption of interstitials, to give excess vacancies for void formation. Outside this volume, equal numbers of defects are present, recombination dominates and no voids are formed. According to Risbet (1974) dislocations with an edge component absorb interstitials preferentially to vacancies in Al and Mg. Screw dislocations are mainly recombination sites in Al but annihilate vacancies preferentially in Mg.

Fig. 9/2 shows a sequence from an irradiation carried out in a Cu .31 Al specimen at 250°C, in which voids can clearly be seen to align along certain dislocations, but not along others. Further research is required to determine the nature of point defect dislocation interactions in Cu/Al foils. Bullough and Perrin (1969) showed that increased overall biasing will decrease the critical nucleus size and the magnitude of the energy barrier for nucleation, thus increasing the nucleation rate of voids and decreasing the incubation time for the formation of voids. As the dislocation density increases, voids appear earlier in the irradiation and in greater numbers. It may be possible to interpret the results in Cu/Al alloys in this manner, in that changes in loop density and climb rate as a function of alloy concentration will alter the biasing factor. However, in foils of Cu 5 at.% Al and Cu 16 at.% Al, the rhombus loops and subsequent dislocation tangle were observed to climb extremely rapidly. This rapid movement of the dislocation tangle (even in very thick foils) was found to occur throughout the irradiation in Cu/Al foils and was associated with the absence of voids.

9.5 Void Swelling After In-situ Annealing of Thin Foils

The effect of an in-situ anneal of thin foil specimens on the subsequent dislocation loop formation in Cu/Al alloys has been discussed in chapter 8. As the annealing temperature T_a was increased, irradiation at a constant T_i reduced the density of rhombus loops. After an anneal at a temperature of about 400°C, a high density of Frank loops nucleated and increased in density until saturation occurred between 520°C and 620°C, depending on the alloy concentration. Fig. 9/3 illustrates the void or dislocation structure which was observed in a Cu 5% Al specimen as a function of anneal treatment. Both areas were irradiated to a total dose of 19 d.p.a. at T_i = 250°C. In fig. (a) rhombus loops nucleated, grew and interacted (in a foil which had not been annealed), so that a continuous climbing dislocation tangle was established. Small loops were

also visible, but no voids were observed. The dislocation microstructure of this specimen has been discussed in this thesis in terms of short range order and on the basis of this explanation, S.R.O. appears to be linked either to the prevention of void nucleation or to an increase in the incubation time. Other specimens of this alloy were initially irradiated at 20°C to build up a high loop density (10^{16} cm^{-3} measured), and then irradiated at 250°C but again no voids were observed. The very high dislocation density formed in this specimen soon reduced in value, to the same magnitude as if the network had been formed at 250°C.

Fig. 9/3(b) shows the resultant void network formed in a Cu 5% Al specimen under the same irradiation conditions, except that it had been annealed for 10 minutes in the H.V.E.M. at 530°C prior to irradiation. Frank loops at a density of $\simeq 10^{16}$ cm^{-3} nucleated and grew slowly in the foil. These loops interacted and a dense dislocation tangle was established, which appeared to be in a steady state condition. Very little dislocation climb was observed to take place, in contrast to the non-annealed specimen fig. 9/3(a). Voids were first visible after a fluence of $\simeq$ 5 d.p.a. and at 19 d.p.a. considerable swelling occurred. Though experiments have not been carried out on Cu 16% Al specimens, it seems likely that void swelling will be observed in this alloy after an anneal treatment. These experiments on the influence of annealed and non annealed foils on void nucleation have been repeated on several different Cu 5% Al specimens with similar results. In the annealed specimens, there again appears the relationship between Frank loop nucleation and void growth. The results may possibly be explained by the fact that disordering of the specimen relieves the internal stress, allowing Frank loops to grow. This implies that internal foil stresses caused by ordering can in some way affect the nucleation of voids.

9.6 Discussion of the Effects of Alloy Composition on Swelling

There have been a number of mechanisms suggested to account for the

inhibition of swelling by impurities. Levy (1974) and Bloom et al (1974) recently emphasized however, that it is not sufficient to consider only how impurities may affect void nucleation or growth. Void formation seems to be invariably preceeded by dislocation loop formation and the development of a dislocation network. It was suggested that the impurities or alloying elements which increase the incubation dose for void formation also increase the dose required for dislocation loop formation. Two possibilities were considered by Levy and Bloom (1974), firstly that the dislocation structure is necessary for void formation and impurities inhibit loop formation or secondly that impurities inhibit both loops and void formation. However, the results from irradiated Cu/Al alloys indicate that impurities do not inhibit loop formation, but reduce the loop growth rate and increase the loop densities.

The main effect of impurities is that a loop character transformation in Cu/Al alloys takes place, which seems to be related to the inhibition of void nucleation. In this respect, impurities are capable of influencing loop formation and growth and subsequently of voids, which leads to a de-emphasis of the class mechanisms in which impurities inhibit only void formation or growth. Void swelling measurements alone, though of technological significance, will not solve the problem of why some materials are more void resistant than others. Thus, future experimental work should concentrate on the early stages of irradiation damage rather than in the secondary void stage.

Impurities may be considered to impede only dislocation climb, thereby limiting the role of dislocations in biasing the defect population Brimhall (1972), or they may change or reduce the strain field of dislocations so they no longer exhibit an appreciable bias towards interstitial capture Norris (1974). Another class of mechanisms involves impurity interstitial Fisher and Williams (1971) Brimhall (1972) or impurity vacancy interactions Smidt et al. (1973), in which the binding energy of

the impurity and the defect is sufficiently high to reduce the effective diffusivity of the defect. If the mobility of either defect is reduced appreciably the recombination rate is increased and both loop and void formation suffer. Schilling and Scroeder (1974) have recently discussed the effects of impurity trapping and point out that the binding energies of substitutional impurities and self interstitials may be large enough to cause trapping, while only interstitial impurities interact sufficiently strongly with vacancies to act as impurity traps. However, the value of $(E_m + E_b)$ for annealed and non annealed foils of Cu 16% Al was measured to be $\triangleq$ .24 eV in both cases, indicating that in Cu/Al alloys, interstitial impurity trapping does not significantly influence void formation. Impurity trapping as a mechanism of void suppression was also tested by Brailsford (1972) for Ni alloys and it was found that the low swelling occurring in some alloys could only be attributable to interstitial trapping if $E_b \triangleq 1$ eV/Atom, which is a very high binding energy.

9.7 Effect of Stacking Fault Energy on Void Formation

The effect of S.F.E. on the nucleation of voids is not clear at present, because other factors may be more dominant. The S.F.E. of Cu/Al alloys has been accurately determined by Ray (1971) and values range from 5 ergs/cm^2 for Cu 16% Al to 40 ergs/cm^2 for pure copper. Energetically, it is more favourable to form faulted loops in the high concentration Cu/Al alloys, but internal stresses prevent this. Weak beam observations of rhombus loops and Frank loops in the non-annealed and annealed foils indicated that both types of loops were widely dissociated, suggesting little change of S.F.E. caused by the anneal. Since the void numbers were radically different after these treatments, the S.F.E. appeared to have little effect on void growth. Moreover, the observations of Adda (1971) on Cu/Ge alloys (which reduce their S.F.E. as the alloy concentration is increased Carter (1975)) indicated that a Cu .5% Ge foil had a void size of 500 Å and void concentration $< 10^8$ cm^{-3}, whereas in a Cu 2.5% Ge foil the corresponding values were 465 Å and 2×10^{13} cm^{-3} (.1%

swelling).

Thus S.F.E. undoubtedly influences the growth rate of loops, to alter the bias, but this effect seems to be a minor perturbation on void swelling, when other metallurgical variables are taken into account.

9.8 Effects of Residual Gases

Gases have been shown to influence void formation in many metals and alloys, by various experimenters, the void swelling being dependent upon the nature and concentration of the species present. The H.V.E.M. is useful as an irradiation facility, because it produces no transmutation effects during the irradiation. However, differences in the void swellings of Pe16 during 1 MeV irradiation by groups at A.E.R.E. Harwell and C.E.G.B. Berkeley were attributed to the presence of hydrogen in those foils prepared at Berkeley, which diffused in from the electropolishing solution. However, hydrogen gas deliberately introduced into Cu 5% Al specimens by electropolishing at high temperatures, did not promote the nucleation of voids even to doses of 35 d.p.a. during irradiation at 250°C. This result is consistent with previous experimental data discussed in this thesis in which hydrogen gas can diffuse out of the foil as the temperature is raised. The results of Fisher et al (C.E.G.B. RD/B/N2727) on Pe16 irradiated at 550°C may be interpreted, if it is assumed that hydrogen has a high binding energy with atoms in stainless steel and that the gas cannot readily diffuse out of the foil.

The presence of an oxide film on the specimen surface may prevent the escape of vacancies from the foil and thus promote the nucleation of the small loops observed in in-situ annealed foils. However, it was not possible to characterize the nature of these defects. A large build up of vacancies in the foil could certainly promote void formation, though this mechanism does not explain the transition from prismatic to faulted loops, as the anneal temperature was raised. Alternatively, the oxide layer may be bombarded into the specimen to provide nucleation sites for

voids and Frank loops. It is difficult to explain by this mechanism, the observed saturation in Frank loop density, since the oxide layer will continually be formed. Non-annealed Cu 5 at.% Al foils irradiated for long periods in the H.V.E.M. would eventually on this basis nucleate Frank loops and voids. This phenomenon was not observed. Foils of Cu 5% Al were also irradiated after having been kept in air for some hours so that a thick oxide layer could form. The resultant loop density was much lower than that observed in freshly polished degassed specimens, as a result of surface contamination stresses. For these reasons, gases or oxide films were not thought to play any significant role on void formation in annealed Cu/Al foils.

9.9 Effect of Precipitation on Void Formation

Hudson et al. (1971) found that irradiated Pe16 Nimonic alloy was very resistant to void swelling and attributed this to the fine coherent γ' precipitate Ni_3 (Al,T_i). Two suggestions were proposed to explain this effect:-

(a) Vacancies and interstitials are trapped at the precipitate surface, without losing their identities and subsequently combine, or

(b) The γ' precipitates inhibit dislocation climb which is necessary in order for the dislocations to continue to be preferential sinks for interstitials.

Williams and Fisher (1972) demonstrated a minimum in swelling as a function of γ' particle size and linked this to mechanism (b). However, in the Cu/Al foils which were immune to void swelling, no precipitates were observed even using high resolution microscopy. Radiation enhanced precipitation also does not seem a likely explanation for two reasons:-

(a) The precipitation effects would occur with or without the anneal treatment.

(b) It is not likely that such precipitation would take place in Cu .31 Al alloys.

9.10 Vacancy Trapping and Short Range Order

The effects of vacancy trapping on void nucleation were discussed by Smidt and Sprague (1973), who suggested that (a) vacancy trapping leads to a reduction in the free vacancy concentration due to enhanced recombination and the formation of vacancy complexes and (b) this reduction in vacancy supersaturation in turn reduces the void nucleation rate. These effects arise from the vacancy interactions with oversize solute atoms, such as Al in Cu. The binding energies could arise from either electrostatic interactions between regions of different electron density or from strain energy interactions. Unfortunately, experimental and theoretical results are neither accurate nor extensive enough to provide insight into the origin or magnitude of binding energies.

Balluffi and Ho (1972) have recently reviewed the subject and concluded that binding energies in aluminium alloys are < .1 eV. March and Rousseau (1971) have also reviewed the binding of solute vacancy interactions in various dilute alloys and the average binding energy from their results appears to be about .25 eV. There have been no accurate measurements of solute vacancy binding energies in Cu/Al alloys, though Wechsler and Kernohan (1959) estimated $E_b \triangleq .6$ eV using resistivity measurements of Cu 15% Al specimens. The authors believed this value to be too high.

An activation energy for interstitial Frank loop growth in thin foils of H.V.E.M. irradiated Cu 16% Al was found to be higher than that in pure copper (chapter 10). The difference was interpreted in terms of vacancy binding with a binding energy of $\triangleq .4$ eV (the vacancy migration energy in Cu being $\triangleq .7$ eV while that in Cu 16% Al $\triangleq 1.1$ eV). A vacancy binding energy of this magnitude is thought to be unlikely for binding to individual atoms, but reasonable for binding to Aluminium clusters. Smidt and Sprague (1973) considered vacancy trapping in a solid solution alloy with vacancy formation energy E_v^F 1.5 eV and vacancy migration

energy E_v^m 1 eV. They found that a vacancy/solute atom binding energy of .4 eV can produce a significant reduction in vacancy surplus and hence in void growth. A search for aluminium precipitates or clusters in Cu/Al foils using high resolution bright field and weak beam images was inconclusive.

The explanation may be linked to the fact that S.R.O. is known to exist in Cu/Al alloys Gaudig (1969). If ordered domains exist, which can locally stress the lattice to promote the nucleation of rhombus loops rather than the energetically more favourable Frank loops, then those domains may influence the void nucleation, by allowing the vacancies to migrate to the domains in an attempt to relieve these localised strains. This is analogous to the fact that single aluminium atoms in a Cu lattice cannot provide the stress to nucleate the Shockley partials Veyssiere (1971), but domains or precipitates may do so. The suppressive effect of the alloy promotes greater recombination of point defects and thus less vacancies to nucleate voids, but more important, could cause the total loop density to be reduced.

When thin foils are annealed in the H.V.E.M., most of the ordered regions disorder, thus relieving the foil stress, to promote the nucleation of a high density of Frank loops. Since the domains are not present to act as vacancy sinks, these vacancies are then able to promote the nucleation and growth of voids. Mazey and Menzinger (1973) suggested that a possible explanation of void inhibition in irradiated Cu-Ni alloys should be ascribed to some other reason than atomic size trapping of point defects and that it was possible, (even though over the whole range of alloy composition, Cu-Ni formed a single phase) a very small scale of clusters of composition different from the matrix may form, the boundary of these clusters acting as traps for vacancies. Clustering extended to nearest neighbours has in fact been detected by neutron diffraction experiments in Cu-Ni alloys.

An alternative explanation proposed by Norris (1974) suggested that atmospheres of over sized substitutional solutes modify the stress field of a dislocation so as to reduce the drift flow of interstitials. This implied a reduction of dislocation preference, which is the driving force for void nucleation. The effect was found to be strong in systems where the impurity atoms remained in solution during irradiation but were surrounded by large strains in the matrix. This theory is not tenable however as an explanation of the resistance to void formation in Cu/Al alloys because the solute atoms would modify the dislocation stress field in the annealed and non-annealed foils.

9.11 Conclusion

Copper aluminium foils of concentration > 2 at.% Al were found to be resistant to void nucleation even after irradiation to doses of 67 d.p.a. Similar foils subjected to an anneal treatment at 550°C prior to irradiation formed voids as rapidly as those observed in pure copper foils.

Various mechanisms for the reduction in swelling due to alloy additions have been considered:-

(1) trapping at solute atoms of the gas atoms necessary for nucleation;

(2) a reduction in vacancy surplus as a result of a decrease in preferential absorption of self interstitials at dislocations;

(3) vacancy or interstitial atoms trapped at solute atoms;

(4) vacancy or interstitial trapping at coherent precipitates;

(5) vacancy trapping as a result of short range order.

The experimental results suggest that at present it is not possible to distinguish between the effects of invisible precipitates or short range ordered domains. As domains have been observed in Cu/Al foils, it is proposed that short range order in these alloys stress the lattice to promote the nucleation of rhombus loops and the suppression of voids.

When the order is removed by high temperature thin foil anneals, the stress may be relieved, so that Frank loops and subsequently voids nucleate.

CHAPTER 10

Growth of Defect Clusters in Copper Aluminium Foils

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10.1 Introduction

The general process in the development of visible defects formed by electron irradiation has two successive stages, nucleation of point defect clusters and their growth. In this chapter, the growth process of loops in copper aluminium foils has been examined.

The growth of interstitial dislocation loops observed in electron irradiated graphite whose radius increased proportionally to the cube root of irradiation time was analysed on the basis of a chemical rate theory by Brown Kelly and Mayer (1968). This same law was obtained by Makin (1969) from the probability estimation of the annihilation of interstitial atoms to sinks of more than one kind, in electron irradiated copper. The cube root growth law observed in gold at room temperature by Yoshida and Kiritani (1973) and in Nickel by Bourret (1971), was analysed as the result of the continual decrease in interstitial concentration by the continuous accumulation of vacancies. All these analyses were thus based on the assumption of the immobility of vacancies.

Norris (1970) observed a linear growth speed for Frank loops in Nickel during electron irradiation at 450°C and this was interpreted as a case in which the vacancies were immobile and the specimen surfaces acted as the dominant sink for interstitial atoms. Wolfenden and Yoo (1974) investigated the growth rates of prismatic loops in electron irradiated Titanium at 450°C and found that loops growing parallel to the foil surfaces had a linear growth rate, while loops inclined in the foil initially grew linearly, but at a later stage in the growth developed a time exponent of $r \propto t^{\frac{1}{2}}$. The authors concluded that the foil surfaces acted as the dominant sink for interstitials, giving rise to the linear growth within the effective foil thickness and that the time exponent reduced to $\frac{1}{2}$ when the loop size exceeded the effective foil thickness.

Chen and Rao (1973) also concluded that surfaces have a significant influence on loop growth in their explanation of a time dependence of

loop diameter $r \propto t^{.7}$, but do not predominate as interstitial sinks over the retained vacancies in the foil.

A constant speed of loop growth has also been reported by Urban (1971) for nickel foils electron irradiated at temperatures between 300°C and 630°C. A detailed analysis, including the temperature dependence of growth speed was given using simultaneous diffusion equations for both interstitials and vacancies. Urban concluded that the loop growth rate was predominantly determined by the mobility of vacancies. More recent work by Kiritani et al. (1975) on interstitial loops formed in Al, Au, Cu, Fe and Mo at elevated temperatures, tends to support this hypothesis.

Depending on the irradiation conditions, especially on the irradiation temperature, point defect clusters can occur as dislocation loops of either vacancy or interstitial type, as stacking fault tetrahedra or as voids. In this chapter, the growth behaviour of interstitial rhombus perfect loops and Frank loops in copper aluminium alloys up to 16 at.% have been investigated over a wide range of temperature and experimental conditions.

10.2 Diffusion Growth Mechanism of Interstitial Loops at Elevated Temperatures

The growth law of interstitial loops proportional to the cube root of the irradiation time at the low temperatures where vacancies are hardly mobile, has been examined in detail by Brown et al. (1969), using the asymptotic solution of the rate equations at large times in a bulk foil, B.K.M. found that

$$\bar{R} \rightarrow \left(\frac{18\sqrt{3}}{4\pi^2 N_1^{\infty}}\right)^{1/3} \theta^{1/3}$$

where $\bar{R}$ = dimensionless loop radius.

N_1^{∞} = limiting value of loop density

θ = $t\sqrt{GS\Omega}$

Since the average loop radius has been defined as

$$\bar{r} = a\bar{R}$$

where a = lattice parameter

then

$$\bar{r} \propto G^{1/6} t^{1/3}$$

(G = generation rate).

Since these calculations were made with the assumption that vacancies are immobile, the cube root growth mechanism will only be observed in bulk foils, irradiated at low temperatures.

This growth law was not observed during experiments performed in copper aluminium foils at elevated temperatures and the mobility of vacancies must be taken into account, in an attempt to explain the observations. When the surfaces dominate all other sinks for interstitials, Norris (1970) calculated that

$$[r = \frac{1}{2} Gh\Omega Z_1 t]$$

where G = defect generation rate

h = foil thickness

Ω = atomic volume

Z_1 = number of atomic sites per loop site.

The growth behaviour of Frank loops in very thin areas of copper foils ($\triangleq$ 1200 Å) was observed to be independent of temperature, by Kiritani et al. (1975) in agreement with this formula, but it cannot explain the temperature variation in growth rate of loops nucleated in thick foils and irradiated at elevated temperatures.

At temperatures where both vacancies and interstitials can more appreciably, the variation of the concentration of interstitial atoms C_I and vacancies C_V under constant irradiation has been given by Kiritani et al. (1975) as

$$\frac{dC_I}{dt} = G - Z_{IV}(m_I+m_V)C_I C_V - m_I C_{SI} C_I - Z_{IL} m_I C_{SL} C_I$$

$$\frac{dC_v}{dt} = G - Z_{IV}(m_I + m_V)C_I C_V - m_V C_{SV} C_V - Z_{VL} m_V C_{SL} C_V \qquad (1)$$

where G = production rate of point defects.

The second terms represent the mutual annihilation by the motion of interstitials and vacancies with mobilities m_I and m_V. Z_{IV} = capture site number for this reaction. The third terms represent the escape of each defect to the foil surfaces, with sink efficiencies C_{SI} and C_{SV}. The fourth terms represent the disappearance of each to the growing interstitial loops, where C_{SL} is the concentration of atomic sites on the dislocations of the loops and Z_{IL}, Z_{VL} are the number of capture sites around one atomic site on the dislocation for interstitials and vacancies.

Computer calculations reveal that initially, both concentrations of interstitials and vacancies increase with G, then the rate of increase of interstitials gradually slows down and starts to decrease as a result of mutual annihilation, diffusion to specimen surfaces and the formation of loops. The vacancy concentration can still increase because of their smaller mobility. This decrease of interstitials and increase in vacancies causes the equal rate of annihilation of vacancies and interstitials. At this time, if the surface sink efficiency for interstitials and vacancies are equal and the loop sink efficiencies are smaller than the surface terms, then

$$[m_I C_I = m_V C_V = \mu] \qquad (2)$$

In this steady state, both types of defects are created and eliminated by mutual annihilation in equal numbers. The defects must also migrate to sinks in equal numbers. Thus to understand loop growth, Urban (1971) postulated that an attractive interaction between point defects and dislocations is greater for interstitials than for vacancies, resulting in a net flow of interstitials to loops. The concentrations of interstitials and vacancies are mainly determined by mutual annihilation and by diffusion to the foil surfaces rather than by capture at dislocation

loops. After substitution of equation (2) in equation (1),

$$\mu = \frac{-m_v C_s + (m_v^2 C_s^2 + 4Z_{IV} G m_v)^{\frac{1}{2}}}{2Z_{IV}} \qquad (3)$$

In thick foils

$$\mu = \left(\frac{G m_v}{Z_{IV}}\right)^{\frac{1}{2}} \qquad (4)$$

The growth speed of interstitial loops is proportional to the difference in absorption of interstitials and vacancies

$$\therefore \frac{dR}{dt} = 2aZ_{IL} m_I C_I - 2aZ_{VL} m_V C_V$$

$$\frac{dR}{dt} = 2a\,(Z_{IL} - Z_{VL}) \left(\frac{G m_v}{Z_{IV}}\right)^{\frac{1}{2}} \qquad (5)$$

Since $m_v \propto \exp(E_{mv}/kT)$ the apparent activation energy obtained from the temperature dependence of growth speed is $E_{mv}/2$. Urban (1971) using his more sophisticated analysis concluded that the apparent 'activation energy' of the climb rate should be higher than one quarter and less than one half of the migration energy of the slower migrating type of point defect i.e. vacancies. Equation (5) has been used in this thesis, to estimate the effective vacancy migration energy from the observed temperature dependence of the growth rate. The measured values are smaller than those determined by conventional methods which may reflect a di-vacancy contribution to the activation energy.

While a diffusion controlled growth mechanism can be used to explain some of the observed loop growth characteristics, the growth behaviours of many loops over a wide range of temperature and specimen microstructure cannot be explained in this manner. If an energy barrier exists for the absorption of point defects at the dislocation core, the climb rate of a dislocation may be controlled by the rate of absorption of point defects, rather than the rate of diffusion of point defects to the dislocation.

10.3 Some Investigations Into Irregular Loop Growth

Before a quantitative evaluation of loop growth characteristics could be made, preliminary experiments were carried out, in order to decide the extent to which external variables contributed to loop growth.

The factors affecting the growth rate of different loops during an irradiation can be divided into two categories. Firstly, those factors affecting the width of the stacking fault ribbon, which may include stress, loop orientation size, temperature and solute impedance. The stress may vary with position in the foil. Loop orientation is a function of both stress and loop size, but the latter should not affect the dissociation width at large loop sizes. These variables are very difficult to analyse and are not thought to affect the loop growth rate to the same extent as those factors in the second category.

The second category includes factors which affect the point defect concentrations contributing to loop growth. These are:-

(1) depth in the foil

(2) position in the beam

(3) proximity of other loops.

Since the H.V.E.M. beam profile is approximately Gaussian in shape, a large variation in loop growth can occur unless great care is taken to ensure that microscope conditions are adjusted to such an extent that the dose rate is constant across the field of view. When care is not taken, the loop growth rate at the centre of the beam can be larger than at the perimeter, causing the loops at the centre to grow rapidly. The loops interact to form a dislocation tangle which may then climb or glide to the foil surface. A common phenomenon at high dose rates is the presence of an outer annulus of small dislocation loops surrounding a central area containing dislocation debris. In the experiments undertaken and reported in this thesis, the greatest care was taken to ensure that only a small part of the beam was used, to ensure a uniform dose

rate.

The wide variation in loop growth rates measured from a small area of a specimen suggested that the position of a loop in a thin foil will affect the measured growth rate. Indeed, this is to be expected from the point defect concentration profiles calculated by Goringe (1971). Since most loops are not parallel to the foil surface, as they grow they encounter regions of differing point defect concentrations, possibly leading to faster growth of some sides.

A zone refined copper foil having a normal F = [111] was irradiated at 210°C and the Frank loop growth recorded as a function of time. Before the loops slipped out of the foil, a thin layer of gold was evaporated onto the foil surface and stereo pairs were imaged on either side of the <211> beam direction. The measurements revealed that those loops parallel to the foil surface but near the foil centre grew at a faster rate than those near the surfaces as shown in fig. 7/30 and this result was used to explain the broad loop size distributions commonly observed in electron irradiated thin foils at elevated temperatures. The loops from which these measurements were made are shown in fig. 10/1 and it was immediately apparent that the size of the inclined loops was much less than the size of the flat on loops. Growth rate measurements were made of all loops in the irradiated area and an average growth rate evaluated for each Burgers vector. The results shown in fig. 10/2, indicate that even though there is considerable variation with depth in the growth rate of loops whose plane is parallel to the foil surface, on average they grew much faster than the three inclined loops. The three Frank loops on planes $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$ and $(1\bar{1}\bar{1})$ are equally inclined at 70° to the foil surface and should grow at the same rate. Referring to fig. 10/1, the inclined loops grew at $\simeq .68$ Å/sec., very much less than the growth rate .93 Å/sec. measured for those loops parallel to the foil surface. The slower growth rate of the inclined loops may

occur as a result of their being nearer to the foil surfaces, though the possibility also exists that preferential growth may be occurring on certain loop planes as a result of internal stresses.

It was noticed that considerable care was needed even with such apparently simple procedures as counting (for densities) and measuring lengths (for size distributions and growth rates). In the case of size measurements, care must be taken over the fact that the images are projections and failure to take this into account correctly can lead to serious error when different loop planes are considered. It was also found, that use of a single 'long diameter' measurement can mask or distort effects which were visible when the loop area was used as a measure of size. Fig. 10/3 illustrates this point and shows that when the long diameters of loops 21 and 22 fig. 10/1 were chosen as a measure of growth rate a linear time dependence was observed (curves 3 and 5). However, when the loop areas were measured and an equivalent radius plotted (curves 1 and 2) both loop growth rates deviated in opposite directions as the loops gradually overlap. These loops, with a measured vertical separation of $\triangleq$ 450 Å commenced to overlap after about 10 minutes of irradiation. At this time, loop 21 which was nearest the electron entrance surface, acted as the dominant sink for interstitials and grew rapidly at the expense of loop 22. The average growth rate for these two loops has also been plotted (curve 4) and shows a linear growth rate indicating that this was a competitive growth phenomenon. Loops 11 and 12 (curves 6 and 7) with a measured vertical separation of 1070 Å and which overlap to a similar extent as loops 21 and 22, showed no deviation in measured growth rates.

Growth rates were also recorded for loops 1 and 2 (fig. 10/1) which were situated near the foil centre but had a vertical separation of $\triangleq$ 90 Å. These loops grew at a constant rate towards each other, until the separation of the nearest loop edges was $\triangleq$ 400 Å. At this point, loop

2 situated nearer the electron entrance surface increased its growth rate at the expense of loop 1. These observations indicate that the loop stress field causes a long range interaction for interstitials, whose magnitude depends on the loop size and horizontal or vertical separation of the loops. When the loops were isolated, linear growth rates were measured, because there were no other loops nearby to act as competitive sinks.

Some interesting growth rates were also measured in a 4000 Å thick foil of 5N copper during irradiation at 205°C and the results are illustrated in figs 10/4 and 10/5. The fastest growing loop (A) was very isolated, while loops (C) and (D), growing at lower rates were surrounded by many other loops. The accuracy of the experimental points on the line defining the growth rate of loop (B) which was extremely deformed suggests that even when a loop is very irregular in shape regular growth can be maintained. After about 36 minutes of irradiation, most of the loops initially present in the foil have slipped to the surface, allowing loops (F) and (G) to become isolated and increase their growth rate. Comparison of micrographs 10/1 and 10/4 show that as the density of Frank loops in copper increases so does the degree of irregularity in the loop shape.

The irregularity of rhombus loops growth has also been investigated. Fig. 7/32 illustrates the growth sequence of loops in a Cu 16% Al foil having some degree of short range order, during irradiation at 170°C. The growth characteristics may be complicated because, in addition to the competition for interstitials, the presence of nearby loops can modify the strain field causing the rhombus loop sides to glide on the {111} planes and thus change the loop shape. Fig. 10/6 illustrates the growth rates of some of the loops imaged in fig. 7/46. In general, rhombus loops grew linearly with time, independent of the alloy concentration or irradiation temperature. However, the presence of nearby loops can

cause the loop growth rates to change as shown by loops (B), (E) and (G). When the interacting loops slip to the surface however, the loops under observation revert back to their original growth rates. As the dose increased, the rhombus loops grew nearer the foil surface which then became an increasingly dominant sink. It was quite characteristic of these loops to cease growing in regions near the surface but to keep growing in directions parallel to the foil surface. This phenomenon can be seen in fig. 10/7.

10.4 A Study of Frank Loop Behaviour in Thin Foils Irradiated After Being Annealed in the H.V.E.M.

An investigation was made into the growth behaviour of Frank loops formed during irradiation in foils cut from fast grown copper aluminium crystals but without an in-situ anneal treatment. The results however were disappointing, because no systematic growth behaviour was observed. The values of the gradient n ($r \propto t^n$) measured from plots of loop radius vs. irradiation time varied from .6 to 1 at each irradiation temperature in the range 120°C to 360°C. The wide variety of results and lack of reproducibility is not surprising, when it is considered that Cu/Al crystals grown at fast rates produced very unreproducible loop density results. There is thus no reason to presume that reproducible results can be obtained until the effects of crystal growth rates, gases introduced during electropolish and short range order, etc., manifested in the 'annealing effect' have been accounted for.

Thin foils cut from slow grown crystals were found to yield reproducible loop densities and also Frank loops after a short in-situ anneal at temperatures between 400°C and 600°C in the H.V.E.M. Frank loop growth rates were thus investigated in Cu 2% Al and Cu 16% Al foils as a function of anneal temperature. The results illustrated in fig. 10/8 are those for Cu 2% Al and indicate that for the same irradiation temperature T_i = 240°C, foil thickness and dose rate, loop growth rates

and log.log gradients decreased as the anneal temperature T_a was increased. The loop growth results in Cu 16% Al showed similar behaviour. The results are summarized in fig. 10/9 for irradiation of a Cu 2% Al specimen, chosen because the loop densities were smaller in comparison to those in a Cu 16% Al foil and thus easier to measure. The experimental points of fig. 10/9 were measured from a single specimen only, which was annealed for 5 minutes at gradually increasing temperatures, with irradiations between successive anneals.

In this particular specimen, the growth rate was linear below the transition temperature of $\triangleq 400^{\circ}C$. In the region of temperature between $350^{\circ}C$ and $450^{\circ}C$ the growth rates of the Frank loops were variable. There was also no systematic behaviour in the time exponent n. The results obtained from this region resemble those measured from the fast grown crystals. Above about $500^{\circ}C$ the value of the exponent n decreased. Two gradients have been plotted for each set of loops measured, the first gradient being representative of loops up to $\triangleq$ 2000 Å in size, while the second gradient occurred when the loops grew above this size. At an anneal temperature of $567^{\circ}C$ for example, the average initial gradient was $\triangleq .7$, changing to $\triangleq .35$ when the loop became deformed, in the later stages of growth. Thus in loop growth experiments in copper aluminium alloys, many values of the parameter n can be measured depending on the internal microstructure of the specimen, itself dependent on the irradiation and in-situ annealing temperatures.

In a further experiment, a foil of Cu 16% Al cut from a slow grown crystal was annealed in the H.V.E.M. for five minutes at $590^{\circ}C$ and then irradiated at gradually increasing temperatures. Measurements of the gradient of log.radius vs log.time were plotted as a function of irradiation temperature fig. 10/10. N was found to be $\triangleq .6$ at $T_i = 240^{\circ}C$, but this increased to about 1 at $T_i \triangleq 320^{\circ}C$. At temperatures in excess of $320^{\circ}C$ for foils of thickness 2500 Å → 3000 Å some loops

shrank while others remained the same size.

Although Frank loops could not be nucleated above about 320°C in foils of 3000 Å thickness, it was observed that loops nucleated at lower temperatures would still grow at 360°C, indicating that loop growth requires a lower supersaturation of point defects than does loop nucleation. At an irradiation temperature T_i = 360°C fig. 10/11, some of the loops were observed not to grow, while other shrink. This effect may occur because at these temperatures the efficiency of the foil surfaces as sinks for interstitials is so large, as to preclude loop growth. Indeed an accumulation of vacancies round the loops can cause shrinkage.

The growth behaviour of Frank loops in pure copper and Cu 16% Al tends to suggest that the controlling factor behind growth, is the mobility of lattice vacancies. In pure copper for example, growth is proportional to the cube root of the irradiation time at room temperature, while at T_i = 100°C linear growth is observed. A similar growth behaviour was observed for Frank loops in annealed Cu 16% Al foils where the exponent $n \triangleq .6$ at 240°C and 1 at 320°C. Thus in general, linear Frank loop growth was not observed, when the vacancy was immobile and steady state conditions not established. The gradual reduction of parameter n fig. 10/9 as T_a increased, can be explained on the basis that as the annealing temperature increased, the loop density increased for the same irradiation conditions. Thus the dislocation line length increased with the consequence that slower loop growth resulted.

10.5 Activation Energies for Vacancy Migration in Copper Aluminium Alloys

The dependence of the growth speed of Frank loops in pure copper on the temperature has been investigated by irradiating a single specimen at different temperatures and averaging the loop growth rates. The loop growth speed as a function of $\frac{1}{T}$ °K is shown in fig. 10/12. At high temperatures where also vacancies are mobile by thermally activated diffusion, the time independent loop growth rate in a sample (which

is sufficiently thick to neglect surface effects) is proportional to exp (E_m^v/2kT). This relation was used to estimate the effective vacancy migration energy from the observed temperature dependence of growth rate.

An activation energy of ≃ .31 eV was measured from the graph, indicating a minimum value of energy for migration of ≃ .62 eV. The obtained values are smaller than those determined by conventional methods which presumably reflect a di-vacancy contribution to D_v, which is understandable considering the high defect concentrations used in the H.V.E.M.

Resistivity measurements made using quenched copper specimens, by Lucasson et al. (1963) and Hasiguti et al. (1965) showed that the vacancy migration energy was ≃ .8 eV. Seeger et al. (1963) and Ramsteiner et al. (1965) found that the divacancy migration energy was ≃ .67 eV. These results are not inconsistent with the activation energy obtained from loop growth rate measurements. The lower limit temperatures for linear growth have been found by Kiritani (1975) to be closely related to the vacancy mobility, especially when the vacancy jump rate is greater than 100 jumps/sec. Since the vacancy mobility activation energy is about .8 eV linear growth of Frank loops in copper has been calculated to be about 90°C in accordance with experimental observations.

An Arrhenius curve has also been plotted for Frank loops in a Cu 16% Al specimen which was annealed in the H.V.E.M. for 5 minutes at 495°C. A gradient of ≃ .57 eV has been measured, to give an apparent vacancy mobility activation energy of 1.14 eV. This value is not inconsistent with a value of 1.08 eV obtained by Lee and Nowick (1956) in Cu 15% Al by a stress relaxation method. Their value for E_m^v in pure copper was ≃ .7 eV.

Since the activation energies obtained from Frank loop growth is consistent with vacancy mobility as the rate controlling process, it

is assumed that Frank loop growth is a diffusion controlled mechanism. Irradiation of Cu/Al alloys at elevated temperatures produced rhombus perfect loops, which remained in this shape throughout growth and had sides lying on the {111} planes, suggestive of low jog densities. Kosel (1975), presented evidence, to show that for rhombus loops in Cu/Al alloys, a minimum damage rate $\phi_{min.}$ was found to be necessary to induce growth at measurable rates. This $\phi_{min.}$ was smaller for alloys of higher stacking fault energy, probably due to the influence of S.F.E. on the energy of jog formation on an extended dislocation. Kosel suggested that, at least in prismatic loops, the climb rate was affected by the rate of jog nucleation rather than controlled by diffusion of point defects to the dislocation. Since linear growth was observed for the rhombus loops at all temperatures and alloys, activation energies for loop growth could be measured. Fig. 10/13 shows typical activation energies for Cu .31 Al, Cu 5% Al and Cu 16% Al alloys. The activation energy measured at high temperatures, region A, for the Cu .31 Al specimen was found to be $\triangleq$ .37 - .39 eV for perfect loops, while measurements of Frank loops in a similar foil, by Imeson (private communication) revealed that the Frank loop activation energy was $\triangleq$ .29 eV. Thus two activation energies have been measured for perfect and Frank loops over the same temperature range in the same alloy. The vacancy diffusion model can be used to explain the Frank loop growth results but it seems unlikely that the activation energy for rhombus loops can be explained in this way.

If however jog nucleation or mobility control the rhombus loop growth rates, then the Arrhenius plot of fig. 10/13 indicates that the energy barrier to be overcome is .37 eV for Cu .31 Al.

One puzzling feature in the graph is the change in gradient with irradiation at low temperatures, which occurs at 150°C. It seems likely that the gradient obtained at the lower temperatures occurs when

the vacancy is immobile, though it is not possible at this stage to explain in a quantitative manner the relevance of the lower activation energy.

Activation energies for the rhombus loops in Cu 5% Al and Cu 16% Al specimens were found to be $\simeq$ .48 eV. and .74 eV. respectively. This latter value for rhombus perfect loops in a Cu 16% Al can be compared to the activation energy of $\simeq$ .57 eV. measured from Frank loops in annealed Cu 16% Al foils.

In the light of the experimental evidence presented in this thesis, it is not possible to decide with confidence whether interstitial loops grow under irradiation by diffusion or jog nucleation controlled processes. However the values of vacancy activation energies obtained from growth experiments of Frank loops agree with other experimental evidence. Secondly, a variation of loop growth time dependence occurred as a function of temperature in agreement with the vacancy mobile model. If the diffusion controlled model is accepted for Frank loop growth, then rhombus perfect loops must grow by another mechanism, i.e. jog nucleation since linear growth of rhombus loops was observed at all temperatures. Also, vacancies cannot have two activation energies, one for each of the loop species. However, it is not known at present whether the activation energy measured for the perfect loop is that of jog nucleation or a combination of mechanisms.

Makin (1971) observed that perfect loops in copper grew at .38 of the rate of faulted loops in the same metal, at 80°C and his climb results indicated that this ratio was nearer unity at higher temperatures. Similar measurements have been made between Frank loops growing parallel to the foil surface and edge on rhombus loops. The results are shown in fig. 10/14. At low temperatures, the rhombus loops grow at a slower rate than the Frank loops, but this ratio reaches unity at about 210°C. At high irradiation temperatures, the perfect loops grow

much faster than the Frank loops. It is suspected that relative rates of loop growth will change with alloy concentration.

This difference in growth rate reflects not only the difference in loop orientation and Burgers vector, but also the different dislocation partial arrangement at the loop edge, which undoubtedly leads to a variation in growth rate.

10.6 Irregular Frank Loop Growth

The irregular growth of Frank loops in specimens cut from fast grown crystals can be contrasted with the much more regular growth of Frank loops in foils annealed at high temperatures. However, in the temperature range $T_A = T_C$ (where T_C is the temperature for transition of the nucleation of rhombus loops to the nucleation of Frank loops) non-reproducible loop growth was observed, with many different time dependences. The growth characteristics of Frank loops growing in fast grown alloys can be compared to the growth of loops in slow grown crystals after being annealed for some minutes prior to irradiation at $T_C \triangleq 400^{\circ}C$.

The Frank loop growth behaviour in the copper alloys was much more complicated than in pure copper foils where only linear growth was observed at the elevated temperatures. Initial measurements were carried out on foils cut from 'fast grown' crystals of Cu 5% Al, Cu 10% Al and Cu 16% Al, in which as many as four different rates of growth were observed for the same loop. For each loop under investigation, area measurements were made and an effective radius calculated. In this manner, a definite pattern of growth was obtained, even for very irregularly shaped loops.

A particular example of this application can be seen in fig. 10/15. A triangular loop growing in a Cu 16% Al foil during irradiation at $T_i = 260^{\circ}C$ (fast grown crystal) grew by the development of additional sides into a very irregular shape, but when the loop area was measured and plotted as an effective radius fig. 10/16, all the experimental points lay on a straight line having a gradient of $\triangleq .61$. The very low S.F.E.

of this alloy causes the Frank partial dissociation separation to be very large, thus stabilizing the loop at large sizes.

Though four separate stages of Frank loop growth have been measured, the second and third stages, denoted by A and B fig. 10/18 have been the most commonly observed. This graph illustrates the growth rates of four loops α, β, γ and δ growing in a Cu 16% Al specimen during irradiation at 280°C, fig. 10/17. Region A illustrates the linear growth of loops α, β and γ after the loops had reached a significant size. In this size range the loops had sides accurately aligned along <110> directions. At a dose of $\simeq 10^{22}$ el./cm.^{2}, the loops developed <112>, <321> and <532> directions and the time dependence also changed to $r \propto t^{.7}$.

The initial loop growth could be interpreted as being jog nucleation controlled, since the loop sides were exactly along <110> directions and these directions have a very low jog density. The Frank partial can also dissociate into a Shockley and stair-rod when the sides are in this orientation. Secondly, the change in growth behaviour occurred when the loops were irregular and with sides along directions which preclude Frank partial dissociation. Loop γ for example is almost circular at the end of the irradiation.

Three factors argue against the jog to diffusion growth mechanism in these loops. The change in gradient occurs at different loop sizes, different degrees of irregularity and at the same value of irradiation time. Apart from the increasing value of dislocation sink strength, the only common factor appears to be the build up of vacancies in the foil. These vacancies may contribute to the slowing down of the growth rate by clustering near the compression side of the Frank loops or increasing the recombination of vacancies and interstitials. Another puzzling feature of the Frank loop growth is the sharpness of the changeover from linear growth to non-linear growth. If vacancies were accumulating in the foil, or if the increasing sink density was causing the reduction

in growth then it would be expected that any transition be gradual. Any change from jog to diffusion controlled growth would imply that if the loops have sides aligned along <112> directions for example then loop growth would be speeded up, rather than retarded. Thus it is likely that vacancies are again controlling the growth of these large Frank loops.

If this mechanism of growth is accepted, then the change of loop shape may be accounted for by the fact that the vacancies attach themselves to loop corners thus changing the line direction to U = <112> and <123>. These particular edge orientations are observed when <110> edged Frank interstitial loops are allowed to anneal in the microscopes.

Fig. 10/18 also demonstrates two other important results. Firstly, the rate of loop growth at small sizes is different to the growth in the later stages of irradiation. It is quite common for Frank loops growing in Cu/Al alloys at diameters < 1000 or 700 Å to grow with a time dependence of $r \propto t^{.3-.7}$. This could be caused by the effect of the loop curvature on growth, but is more likely to be the results of non-steady state conditions, during the initial stages of growth. Loop γ is a typical example of a loop which developed three different growth rates at various periods in its career. Secondly, Frank loops on planes inclined to the foil plane can grow with time exponent > 1. Loop δ, for example is edge on to the beam and commences growth linearly. As the loop approaches the surface, growth ceases along these edges moving towards the surface and rapid growth $r \propto t^2$ takes place at right angles to this direction.

The growth mechanism has however been further complicated by the fact that Frank loops growing on planes parallel to the foil surface can grow at a rate greater than unity. Fig. 10/20 demonstrates the growth rate of a Frank loop in a foil of Cu 5% Al irradiated at a temperature of 308°C. Fig. 10/19 illustrates the loop in its various

stages of growth. At the commencement of irradiation, the loop grew rapidly with a gradient of 2.6, but the growth rate continually reduced until $r \propto t^{.87}$ when it was so large, that it slipped to the foil surface. Unfortunately, there is no mechanism of growth available at present to explain this phenomena.

The fourth stage of growth is not observed very frequently but occurs after a long period of irradiation, when the growth rate changes to a region of zero growth. On the few occasions when this behaviour was observed, the background dislocation structure had been reduced to low levels, by slippage to the foil surface. The growth of the loops was probably restricted by the very high accumulation of vacancies in the foil.

10.7 Climb Mechanism of Rhombus Loops

Weak beam micrographs of dissociated Frank and prismatic loops indicate that growth results from the formation and mobility of jogs, or constrictions, along the extended dislocations. It is possible to observe these super jogs moving rapidly round the loops as a ripple effect during irradiation experiments in the H.V.E.M. if high dose rates and magnifications are used.

A unit jog on an undissociated edge dislocation is a step in the extra half plane of atoms above the slip plane; the dislocation on one side of the jog lies in a slip plane one interplanar distance higher than the other side of the loop. A row of interstitials added to the edge of the half plane produces a pair of jogs of opposite sign as does the addition or emission of a row of vacancies. The emission of interstitials from a dislocation is difficult, because of the high energy of formation. Jogs of the same sign may combine to form superjogs of height greater than one interplanar spacing. Calculations Carter (1975) suggest that dissociated dislocations will be at least partially constricted at a jog causing cusps in both partials. Since the separation

of partial dislocations in Cu/Al alloys is less than 150 Å, it is not possible to image constrictions using bright field images. Weak beam micrographs have been taken of Frank loops and perfect loops, although considerable difficulty was experienced, because of the depth of these defects in the foil. Carter (1975) provided evidence to show that most of the constrictions found on dissociated dislocations in homogeneous alloys were caused by jogs on the dislocation line and that the jogs would be partially extended, to a degree depending on the jog height and the S.F.E. of the metal.

If we consider a pair of opposite sign superjogs on an undissociated edge dislocation, which can then dissociate, the superjogs will also tend to dissociate, forming an extended superjog pair as shown in fig. 10/21(A). It is assumed that all the faults are intrinsic and that the dislocation segments not on the original glide plane are dissociated on the other {111} plane containing the Burgers vector. The original dislocation on the γ plane had a Burgers vector of $\overline{BA}$, which then dissociated into $\overline{B\gamma} + \overline{\gamma A}$ Shockley partials. The acute angled jog has a stair-rod dipole corresponding to a row of $\frac{1}{3}$ vacancies, with opposite Burgers vectors $\overline{\gamma\delta}$ and $\overline{\delta\gamma}$ of the type $\frac{a}{6}$ <110>, while the obtuse jogs corresponding to a row of $\frac{1}{3}$ interstitials has a stair-rod dipole with opposite Burgers vectors $\overline{AB}/\delta\gamma$ and $\overline{\delta\gamma}/AB$ of the type $\frac{a}{3}$ <100>. The line tension of the stair-rod dislocations pulls the Shockley partial dislocations together at the jogs to produce a partial constriction.

The mechanism of jog formation on an extended dislocation is not well understood, mainly because of the difficulty in observing jogs. Several models have been suggested by Stroh (1954), Barnes (1954), Kimura et al. (1959), Thomson (1962) and Escaig (1963). According to the model by Stroh, the formation of a constriction in the dislocation is necessary, by pinching together Shockley partials to form a perfect dislocation, which may then climb by the formation of a jog pair as

shown in fig. 10/21(B). The energy of such a constriction consists of the work done in forcing Shockley partials together and is given by Friedel (1964) as

$$W_c = \frac{\mu b_p^2 d}{30} \left(\ln. \frac{d}{b_p}\right)^{\frac{1}{2}}$$

where μ = shear modulus, taken as 5.5×10^{11} dynes

b_p = Burgers vector of partial 1.47 Å

d = equilibrium width of separation.

Observation of the extent of dissociation of a perfect loop into its component Shockley partials reveals that the splitting is very much smaller than calculated. This may be due to the small loop size, non equilibrium growth conditions, impurity pinning or segregation of solute to the stacking fault. If the separation is assumed to be 120 Å in a Cu 10% Al alloy, the constriction energy has been calculated to be 6.23 eV. Since one constriction is required on each side of the jog, the energy necessary for jog formation is $2W_c$ i.e. 12.45 eV. in the absence of stress.

The energy of the extended jog pair is the sum of the energies of stair-rods, Shockley partials and extra area of stacking fault. The Shockley jogs may be assumed to have only the energy associated with the core, because they are very short and the strain fields are lost in those of the dipoles. If the two jog lines are close together, the Shockley strain fields cancel each other. According to Hirthe and Lothe (1968), the self energy of a jog can to a first approximation be given by the core energy, thus

$$W_f = \frac{\mu b^2 d}{4\pi(1-\nu)}$$

The energy of an extended jog pair is given by

$$W_{jp} = \frac{3\mu d}{8\pi}\left(2b^2_{\gamma\delta} + 2b^2_{AB/\delta\gamma}\right) + \frac{3\mu d_{(111)} b_s^2}{8\pi}$$

where $b_{\gamma\delta}$, $b_{AB/\delta\gamma}$ and b_s are the Burgers vectors of stair-rod and Shockley dislocations.

Thus to a first approximation the energy for a separation of 120 Å is W_{JP} = 21.5 eV, though partial constriction will decrease this further. These activation energies are rather high, suggesting that loop growth by the movement of constrictions is a difficult process.

Other models suggested by Thomson, Escaig and Friedel include the nucleation of a triangular step on the stacking fault ribbon as shown in fig. 10/22, in which the dipoles extending across the fault are of stair-rod type. The dipole $\delta\gamma$ - $\gamma\delta$ moves one row to the left, with the absorption of each point defects. The first point defects produce the short jogs $\overline{B\delta}$, $\overline{\alpha\delta}$ and $\overline{B\alpha}$ in addition to the increase in stair-rod dipole length, though the energies equivalent to the core energies will be small. The triangular configuration would grow until it reached the opposite side of the extended dislocation, to form a double jog line fig. 10/22(c). Thomson and Balluffi (1962) also suggested that a row of point defects along one of the Shockley partials of an extended dislocation may be considered as a small prismatic loop, which may dissociate to form an extended jog pair. This model discussed by Hirthe and Lothe (1968) is shown in fig. 10/23. In this configuration, the partials $\overline{\gamma A}$ and $\overline{B\gamma}$ repel each other, though the net interaction of the $\overline{\gamma A}$ dipole may be small, when the dipole is closely spaced. The jogs $\overline{B\delta}$ and $\overline{\delta A}$ do not interact very strongly and probably do not provide much force to extend the configuration across the fault against the stair-rod dipole line tensions. However, when the height and separation of the jog pair is large, the Shockley stress fields not not overlap. Thus at some critical separation, the loop dissociates to form an extended jog pair.

A schematic diagram of a dissociated rhombus perfect loop is shown in fig. 10/24(A), in which stair-rods $\overline{\gamma\delta}$ and $\overline{\gamma\delta}/_{AB}$ link the

Shockley partials $\bar{\gamma}\bar{A}$ and $\bar{B}\bar{\gamma}$ at the intersection of the {111} planes. When the loop is small, the repulsive interactions between Shockley partials on opposite sides of the fault are partially cancelled by the attraction of the Shockleys on the other side of the loop. Thus, small loops should not be extended to the same extent as large loops, or isolated edge dislocations of the same Burgers vector. It has not been possible, even with the weak beam technique to image the stair-rods at the loop corners, mainly because of their small size and projection in the foil. Fig. 3/24 shows an enlargement of rhombus loops, in which the Shockley partials and associated stacking faults are clearly visible. Most of the loops have several partial constrictions along each side.

Carter (1975) has reviewed the theories of Nabarro, Friedel and Jossong (1967) concerning the extent to which jogs on extended dislocations can be constricted and concluded that the extent of the dissociation depends on several factors, including the S.F.E. of the metal and the height of the jog. Jossang (1967) represented an extended jog on a dissociated edge dislocation by a piecewise construction of twelve straight segments and deduced the constriction energy and jog extension for jogs of different height.

The important conclusion from this work, was that jogs are always extended to some degree and that the extension is greater at a given height, the lower the S.F.E. of the material. Calculations performed for silver, having a S.F.E. of 17.5 ergs./cm.^{2} and a stair-rod dipole of $\bar{b} = \frac{a}{3}$ <001>, revealed the dissociation width of the jog to be about 11 Å. For a Cu 16% Al, having S.F.E. $\simeq$ 5 ergs./cm.^{2} and an acute stair-rod dipole of $\bar{b} = \frac{a}{6}$ <110>, the extent of the dissociation would be expected to be much larger. Fig. 5/32 shows constrictions along the sides of dissociated prismatic loops, which appear to be partially extended, though, if the constrictions are joined by an extended jog,

the stair-rod dipoles are out of contrast. Fig. 10/26.

Once formed, jogs can move along the dislocation by absorption of interstitials, though this process is not well understood. However, it is likely that the activation energy for jog mobility will be lower than that for jog formation, unless constrictions are necessary before absorption or emission can take place. In the case of a jog line, absorption of a point defect does not result in any change in the jog configuration except that it is moved one step. However, absorption of a point defect to extended superjogs would involve the creation of extra lengths of stair-rod dislocation which may proceed by a similar mechanism to that of jog nucleation. It is suspected, that dislocation loops which are not dissociated to any significant extent and whose jogs are not extended may have little difficulty in jog nucleation and may grow by a diffusion mechanism.

The rhombus loops are observed to be straight sided during growth, indicating a low jog density. In general, rhombus loops imaged under weak beam conditions had two or three partial constrictions, indicative of jogs along each loop side; the jog spacing being controlled by the rates of jog nucleation and mobility. When the rate of jog nucleation is less than the rate of mobility, then jogs move along the sides to the corners before new jogs are nucleated and each jog then contributes one layer to the loop side.

It is likely that jogs nucleate at the loop corners, since the presence of stair-rods there probably results in partial constriction of the stacking fault ribbon, which would favour jog nucleation. This is illustrated in fig. 10/24(B) and demonstrates that nucleation of a jog at the corner would require the formation of only one stair-rod dipole, rather than the two dipoles which are required to nucleate a pair of jogs on the loop side.

Two cases can give rise to a constant growth rate. Firstly, the

jog motion is very fast and nucleation is concentrated at the corners. Secondly, jog nucleation may occur along the loop sides at a rate great enough to ensure that they do not have time to travel to the loop corners before new jogs are nucleated, though in both cases, the loop growth rate is proportional to the rate of jog nucleation. Since it has not been possible to observe the process of jog nucleation and motion the actual mechanism of growth is uncertain. The jogs probably move by absorption of interstitials with a lower activation barrier than that for jog nucleation, though it is not certain whether they nucleate preferentially at loop corners.

A modified jog nucleation model requiring a low activation energy has been proposed by Grilhe et al. (1977). This model assumes that a row of point defects in the vicinity of two Shockley partials may be considered as a prismatic loop which itself can dissociate. The extended jog pair may be developed by glide when a critical jog size (dependent on S.F.E.) has been reached. Weak beam studies of rhombus loops during growth are needed before their theory can be substantiated.

10.8 Growth Mechanism of Interstitial Frank Loops

Large regular hexagonal Frank loops were rarely observed in electron irradiated Cu/Al alloys. Instead, polygonal loops with edges along <110> directions were imaged. The loops developed these <110> edges as they grew from the original cluster because a $\frac{a}{3}$ <111> dislocation lying along <110> can lower its energy by dissociation (using the Thompson notation) of the type:-

$$A\alpha = A\gamma + \gamma\alpha$$

In an isolated hexagonal interstitial loop three alternate sides dissociate so that the resulting Shockley is above the loop plane and the three remaining sides dissociate below the loop plane. Only the obtuse angled dissociation has been imaged though Gaboriaud (private communication) has calculated that extrinsic dissociation (acute) of

small interstitial loops is favourable in silicon.

During growth of the loop, condensation of interstitials can occur only by the nucleation of jogs which in general is likely to be a difficult process because it involves an increase in the dislocation line energy. Moreover, jog nucleation will tend to increase in difficulty as the ribbon width between the Shockley partial and stair-rod dislocation increases. However, Shockleys at interstitial loop corners (with the exception of the 300° corner) are constricted and are thus expected to be favourable sites for jog nucleation. Further, interstitials can condense on the newly formed jogs, which therefore propagate along the sides of the dissociated Frank loop. If jog propagation is relatively easy, the regular hexagonal shape will be maintained. However, if a particular corner ceases to accept interstitials (e.g. the arrival of an impurity atom at the corner) then other polygonal shapes may be expected to develop from the initial triangular or hexagonal shapes which predominate when the Frank loops are small.

Fig. 10/25 illustrates the dissociation of a Frank partial dislocation in a Cu 10% Al foil into its component Shockley and stair-rod dislocations, imaged using g <113> at a <110> beam direction. This loop commenced life with a triangular shape and has subsequently changed shape. No dissociation can be observed along directions which are not along <110> as can be seen at F where $\bar{U} = [2\bar{3}1]$ or at G where $\bar{U} = [1\bar{2}1]$. The line direction of the dislocation segments joining the constricted Shockley partials at B or D for example, appear to be the same as that of the side to which they are moving. Jogs also appear to be moving in two opposite directions along the side AG, with B moving towards A and D moving towards G. This particular triangle irradiated at about 240°C is also in the process of nucleating extra sides along <112>, <123> or <532> directions thus increasing its irregularity. The additional ledges on the loops are probably caused by impurities in the

foil and the high concentration of vacancies in the vicinity of the loop.

Some possible mechanisms of growth are shown in fig. 10/26 (B) (C) and (D). Fig. (C) schematically illustrates the growth mechanism observed along the loop edge AG in fig. 10/25. The direction of the sides on either side of the constrictions are <110> implying that dissociation must occur, to reduce the loop energy. If the extra length of side is along the <123> direction, no dissociation can occur and the side will have a very high jog density as shown. Interstitials may attach themselves at the corners causing the partial $D\gamma$ to shorten and move to the right. This seems to be the most commonly observed method of growth in the Cu/Al alloys at large loop sizes.

When the loops are small, or have sides accurately aligned along <110> directions then mechanism (D) may apply. The jog direction is along <110> and depending on the jog size, may be able to dissociate onto the inclined β $(1\bar{1}\bar{1})$ plane. Unless the corner has an angle of 300°, complete constriction of the Shockley partials must occur. If the length AB is small, then it is unlikely that dissociation will occur and interstitials can attach themselves at point B to move the Shockley constriction towards the right. When the jog AB arrives at the corner of the loop, a new length along <110> will have been created. Fig. (B) shows the dissociation reaction expected to occur when the angle of the jog to the original line is 300°. This particular reaction was only observed twice and it has been established that such a corner allows a stair-rod (in this case $\gamma\alpha$) to link the dissociated Shockley partials. The acute corner under normal circumstances would be expected to constrict the Shockley partials, but the effect of $\bar{\gamma}\bar{\alpha}$ appears to increase the width of the dissociation of $\bar{D}\bar{\alpha}$ and it is likely under these circumstances that the line tension of $\bar{D}\bar{\alpha}$ will cause a stair-rod to form at the intersection of the α and γ planes, at point E.

The experimental results suggest that Frank loops grew by movement of constrictions along the sides, except in very special situations. One such case can be seen in fig. 10/27(A) in which the dissociation for this Frank loop in Cu 16% Al is anomalously large as to make constriction very difficult. The arrangement of dislocations can be seen in fig. 10/26(A). One possible explanation of this very large dissociation is that at an earlier stage in the irradiation two loops have amalgamated, one on the inclined plane and the other parallel to the foil surface. What is now observed as a dissociation, may have been a dislocation loop on an inclined plane. Fig. (B) shows an interesting example of a dissociated Frank loop (the stair-rod is not in contrast), whose Shockley partial is constricted at several places and whose distance between constrictions increases from one corner of the loop to the other. This phenomenon might be interpreted, if the propagation of jogs is slow along the original edge of the loop and that additional jogs form at the corners and propagate more readily then the leading jog along the edges, catching up with the jogs ahead. If jog propagation is slow, the loop size determines the number of constrictions. Thus fig. (C) shows a small Frank loop without any constrictions along its length, indicating that in this particular loop jog propagation is rapid and that jogs have time to cross the loop side before another is nucleated. Fig. (D) shows a larger loop with two constrictions and again, an increasing distance between them as the distance along the side increases.

A variety of Frank loop shapes have been observed in Cu/Al alloys, ranging from triangles to loops with twenty sides. At intermediate loop sizes, the common defect appeared to be the irregular hexagon. Frequently, Frank triangles were observed to nucleate and grow, then subsequently transform into polygonal shaped loops, by the blunting of each acute corner in succession. This configuration can be observed in fig. 10/28 for a copper specimen irradiated at 280°C. Initially the

loop grew as a triangle as in (a), but when the side lengths reached about 1200 and 1300 Å, one corner blunted. After further irradiation a second and then a third corner blunted to produce an irregular hexagon. Continued growth causes the nucleation of edges which are not aligned along <110> directions. The shape of the loops in pure copper can be contrasted with the very irregular shapes as seen in for example Cu 5% Al fig. 10/19. The difference may be due to the increased dissociation separation, the presence of solute or the difference in mobility of vacancies.

Fig. 10/29 (A) (B) and (C) shows a possible mechanism for growth of the polygonal loops. Fig. (A) illustrates the dissociation at the acute corner where complete constriction of the Shockleys is expected to occur. This assumption is based on the fact that triangular loops anneal at a similar rate to polygonal loops having obtuse corners. Weak beam micrographs of triangular loops did not reveal any stair-rod linking the Shockleys at the intersection of the dissociation planes. Continued growth of the triangle allows a small undissociated segment $\bar{D}\bar{\delta}$ to grow, which on reaching a significant size will also dissociate into its component Shockley and stair-rod dislocations.

Loops α and β fig. 10/30 show an interesting growth sequence in a Cu 16% Al foil. Loop β can be observed to nucleate as a triangular defect but change rapidly through a series of shapes into a nine sided figure, at which time a dislocation Frank loop interaction caused a shear of the stacking fault. Fig. 10/29 (D) shows the resultant dislocation configuration, made up of Shockley partials $\frac{a}{6}[11\bar{2}]$ and $\frac{a}{6}[\bar{1}2\bar{1}]$ on the (111) plane, perfect dislocations $\frac{a}{2}[110]$ and $\frac{a}{2}[101]$ resulting from the shear process and the original dislocation with $\bar{b} = \frac{a}{2}[01\bar{1}]$. It is interesting to observe that some of the stacking fault in the original Frank loop remains, after the transformation has occurred. This reduction of Frank loop density by interaction with

moving dislocations is very commonly observed in copper aluminium foils.

A variety of loop shapes has also been reported in quenched metals, along with calculations of the elastic strain energy of such dislocation loops. Bacon and Crocker (1965) derived the elastic energy of several different regular n sided loops. Jossang and Hirth (1966) computed the energies (elastic plus stacking fault) of regular and truncated stacking fault tetrahedra using a similar procedure. A general formulation developed by Jossang et al. (1965) and De Wit (1967) computed the elastic energy of dislocation configurations formed from piecewise straight segments (the dislocation core was not included). De Wit found that the total elastic energy of the loop decreased rapidly for small amounts of truncation at the vertices and that for similar loop areas, the triangular configuration always had a higher energy than the pentagon, hexagon or octagon. Thus De Wit predicted for undissociated loops a series of shapes from triangle to circle and a smooth reduction in the energy as the loop progressed towards the circular configuration. This prediction agrees with the experimental observations that triangles proceed by a series of transformations into complex 'n' sided loops. However, the circular shape has not been achieved during loop growth of low stacking fault metals, because dissociation of the Frank partial occurs to reduce the loop energy.

A comparison of the energies of dissociated vacancy Frank triangles, hexagons and non dissociated circles has been computed for a series of Cu/Al alloys by Gaboriaud and Grilhe (1972), having a range of $\frac{\gamma}{Gb}$ from $.7 \times 10^{-3}$ to 5.8×10^{-3}. For values of $\frac{L}{b} = 50$ upwards, (where L = side length and b = Burgers vector), the triangular defect always had a higher energy than the hexagonal defect. These results demonstrate that the Frank triangle is in a metastable configuration. One possible reason is that impurities may be pinning the loop corners, secondly,

the loops may plate out to form triangles from the initial nucleated cluster and an energy barrier may have to be overcome before the lower energy polygonal loop shape can form. Thirdly, different orientations of triangle on the (111) plane parallel to the foil surface were observed at the top and bottom foil surface. In the foil centre various irregular hexagonal configurations were observed. There is evidence to suggest that the depth of a Frank loop in a foil can affect the final loop orientation.

10.9 Conclusion

The growth rates of Frank and rhombus perfect loops have been studied in various Cu/Al alloys irradiated over a wide range of temperatures. While linear growth rates were measured for perfect loops growing under all irradiation conditions, very non-reproducible growth rates and loop densities were observed in specimens cut from Cu/Al alloy crystals grown in a vacuum furnace at fast rates (2.2 cm/hr). However, when specimens were cut from slow grown crystals no Frank loops were observed to grow, until the foils were annealed prior to irradiation in the H.V.E.M. When this was done, the loop growth rates and densities were much more reproducible, but still just as difficult to understand. These characteristics of radiation damage have been attributed to short range ordering though the possibility of sub microscopic precipitates affecting growth has not been ruled out.

Non linear growth rates have been observed in all the alloys, whose time dependence n varied between .33 and 2.6. Igata (1975) also observed an $r \propto t^{.55}$ growth rate in N_b 1% M_o and N_b 1.7% Z_r after irradiation at 200°C, but linear growth for pure N_b irradiated under the same conditions.

The fact that different activation energies were measured for rhombus and Frank loops growing in the same alloy indicates that a different growth mechanism is applicable to each loop. The experiments suggest that Frank loops grow by a diffusion limited mechanism, while

the rhombus loop growth rate is controlled by the movement of jogs along the loop edges. On the basis of a diffusion limited growth rate, the vacancy migration energy is given by twice the loop growth activation energy. Thus values of $\triangleq$ .62 eV and 1.14 eV have been measured for Cu and Cu 16% Al respectively, though there is evidence that the multiplying factor is $\triangleq$ 2.5 instead of 2, caused either by the effect of divacancies on loop growth or a binding energy between vacancies and impurity atoms in the foil.

This difference in growth behaviour of loops in Cu/Al alloys may follow from the arrangement of the dissociated partial dislocations. Preliminary results tend to suggest that dissociated Frank loops grow by the movement of constrictions, commencing from the loop corners. Very little evidence has yet been gathered concerning the growth characteristics of rhombus loops but results indicate that few constrictions appear along each loop side and that the jogs may be extended in the form of stair-rod dipoles. These jogs may be difficult to nucleate, with the effect that the growth mechanism of rhombus perfect loops is very different to that of Frank loops.

The wide variety of loop shapes and growth rates are not yet understood but have been attributed to the effect of such variables as impurities, vacancies, foil thickness, stacking fault energy, dose rate, temperature, depth of defect in foil etc. If loop growth experiments are to be used as a means of determining the dislocation bias term (the preference of dislocations for interstitials rather than vacancies) then the effect of these external variables must be completely understood. To this end, computer calculations and experiments are being carried out by D. Imeson (D. Phil thesis Oxford) on Cu/Al alloys taking into account specimen surfaces, vacancies mobility and the dissociation of di-interstitials. Particular attention is being paid to (1) growth rates of crystals, (2) in-situ annealing treatments, (3) jog and diffusion controlled loop growth mechanisms.

CHAPTER 11

Summary and Suggestions for Further Work

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Introduction

The behaviour during 1 MeV electron irradiation of the Cu/Al alloys was found to be markedly different from that in pure copper under similar conditions. During H.V.E.M. irradiation of copper, loops nucleate when irradiation commences and, after a short time, there is no further loop formation. The loops formed are mainly of Frank type, which at a later stage unfault to produce normal perfect dislocations. In thick foils, the loops grow to form a dislocation network, which after further irradiation supports the formation of voids. The aspect of radiation damage that is least understood, is the influence of alloying elements on the behaviour of materials under irradiation. In this thesis are reported the results of in-situ irradiations in a H.V.E.M. of various copper aluminium alloys.

11.1 Loop Nature

Several types of loop were observed during irradiation, the nature depending on the alloy concentration and the specimen preparation. In specimens cut from slowly grown crystals and electropolished at low temperatures, the loop nature changed from Frank in the pure copper to rhombus perfect loops with $b = \frac{a}{2}\langle 110\rangle$, lying on planes near {110} in those Cu/Al alloys of aluminium concentration > 2 atomic percent. The formation of perfect loops can occur when two Shockley partials separated by one atomic layer clear the Frank loop fault to leave a hexagonal perfect loop on the {111} plane, which can then rotate by a process of glide and climb to a {110} orientation. However, the rhombus loops in the Cu/Al alloys appear to be perfect even to very small sizes, which suggests that another mechanism may promote the nucleation of these defects. Clearly there is a need for further investigation into the mechanism of nucleation of these loops using high resolution weak beam microscopy.

Foils of concentration > 2 atomic percent aluminium cut from

crystals grown at fast rates nucleated a mixed population of Frank and perfect loops whose densities were not reproducible from one slice to another. The technique of specimen preparation was found to be important if consistent results were to be obtained. In particular, it was found necessary to electropolish specimens at very low temperatures $\simeq -70^{\circ}C$, to prevent the diffusion of gas (presumed to be hydrogen) into the specimens. One effect of gas diffusion, was the nucleation and growth of dipole type perfect loops with directions parallel to <112>. Another important effect of variations in electropolish temperature was (depending on the alloy concentration) the variable high density of small perfect loops which formed even at very high temperatures in the alloys. One major conclusion of this work has been that if quantitative radiation damage results are to be obtained from H.V.E.M. observations, then particular attention must be paid to the specimen preparation, otherwise anomalous results will occur.

11.2 Weak Beam Investigation into the Structure of Interstitial Loops

The structure of the irradiation produced Frank and perfect loops has been examined using weak beam imaging conditions. Frank loops grown in foils cut from fast grown Cu/Al crystal were imaged in g <113> $\bar{z}$ <110> to reveal the Frank partial dissociation into Shockley and stair-rod dislocations, the dissociation width depending on the S.F.E. Computer calculations of the expected contrast have been performed by Holmes (1975), which agree with the experimental results for alloys of concentration < 10 at.% Al. However, considerable deviation from the calculated values of dissociation width were observed for the Cu 10% Al and Cu 16% Al alloys, which is likely to be due to a solute dislocation interaction. The effect that metallurgical and thin foil parameters have on the dissociation of the Frank partial dislocation in these alloys needs to be investigated. Further, the weak beam

technique could usefully be applied to vacancy Frank loops in quenched Cu/Al foils. These loops could be more easily investigated than interstitial loops since much thinner foils could be used as a result of the absence of the denuded layers. Experiments also revealed, that while loop sides aligned along <110> directions dissociated, those along <112>, <321> or <532> directions were not able to do so.

High resolution micrographs using weak beam diffraction conditions to investigate the structure of rhombus perfect and elongated perfect loops showed that the perfect dislocation dissociated into two Shockley partials. The method of elongated loop formation is not yet understood though it is suspected that hydrogen precipitation along <112> directions may be responsible for the defect. An area of research offering exciting possibilities is the observation of the growth and anneal of loops in the H.V.E.M. using weak beam imaging conditions. Preliminary investigations in this field have indicated that under suitable conditions, ripples can be observed running along the loop sides. An investigation could also be made into the interaction of point defects and dislocations using weak beam in the H.V.E.M., since micrographs taken in the H.V.E.M. at 250°C have shown clearly the dissociation of dislocations in Cu 10% Al into their component Shockley partials.

11.3 BKM Theory and Application to Thin Foils

The chemical reaction rate theory of Brown, Kelly and Mayer (1969) which was modified by Goringe (1971) and Hossain (1974) has been used to explain the loop nucleation observations. These theories are thought to be fundamentally correct for temperatures up to $\simeq$ 200°C above which, the di-interstitial is thought to dissociate. Below this temperature, experimentally measured densities were corrected to bulk and activation energies of interstitial migration (.13 eV) and interstitial solute binding energies of (.11 eV) were measured from the Arrhenius plots of ln. (density) vs $\frac{1}{T}$ (absolute temperature).

At temperatures in excess of $\simeq 200^{o}C$ the BKM model has been modified by Bourret (1970) to take into account the di-interstitial instability. The correction factors Goringe derived were only applicable to the case of a stable di-interstitial and corrections for thin foil effects were made at the higher temperatures with strong reservations. With this reservation in mind, an apparent dissociation binding energy of $\simeq .65$ eV was measured.

Other measurements made, included depth distributions, defect size distributions and denuded zone widths. The diffusion of interstitials to the foil surfaces was found to affect these parameters significantly. When loop size distributions were considered, it was found that in addition to the spread produced by depth variations, two further effects were noted: (i) a number of slowly growing defects were nucleated late in the irradiation and (ii) a number of large interstitial loops coalesced to form even larger defects. It is thus unlikely that the very narrow distributions implied by nucleation theory will be observed during in-situ electron irradiation studies. The results indicate that studies are accurate under specified conditions:- at temperatures $< 200^{o}C$ and at the foil centre. More detailed rate theory computer calculations are being performed by Imeson (D. Phil. Oxford), in which both the vacancy and interstitial defects are assumed to be mobile. The effects of mobile di-vacancies are being considered, along with the dissociation of the di-interstitial.

11.4 Annealing Effect

Changes in the loop nature and density were observed in thin foil specimens irradiated after suitable pre-anneal treatments in the microscope. The changes that take place in the radiation damage structure are so dramatic, as to warrant further investigation in Cu/Al alloys and in other commercial alloys. A particular example of this effect is that prior to in-situ anneal, irradiation of a Cu 10% Al foil

at 250°C will nucleate a low density of rhombus perfect loops. After an anneal in the microscope for 10 minutes at 550°C, a similar area was found to nucleate a very high density of Frank loops. At present, the behaviour though complicated, is well determined in Cu/Al alloys but a satisfactory explanation of this effect has not been obtained. One possible explanation lies in a short range ordering mechanism, since Cu/Al alloys are prone to this type of order. Since S.R.O. is a highly localised phenomenon, with atomic correlations rarely extending more than a few unit cells, it has been found difficult to study and interpret. The conclusion tentatively reached in this thesis is that S.R.O. initially in the foil is destroyed during an in-situ anneal. However, further work needs to be carried out to confirm this mechanism or determine whether dissolved gas complexes, precipitates or a combination of all three causes the transition.

Experiments performed on all the alloys revealed that the effect occurred in those alloys of concentration in excess of .31 at.% aluminium. The transition temperature of $\simeq$ 420°C was observed to be common to all the alloys. Though precipitates were not detected in the non annealed specimens, a domain like structure similar to that observed by Gaudig (1969) in a short range ordered foil of Cu 15% Al was observed.

11.5 Void Formation in Cu/Al Foils

S.R.O. has been invoked as one of the possible causes of low swelling rates during irradiation and this has been found especially true in Cu 15% Al by Adda (1972). This view has been reinforced by experiments carried out for this thesis on the formation of voids in Cu/Al alloys. The net effect of increasing Al content was a drastic reduction in void swelling at all irradiation temperatures and the void swelling was reduced to zero when the aluminium content was > 2 at.% (rhombus perfect loops were the predominant defect). The reduction in void swelling caused by the Al additions might be explained by vacancy

or interstitial trapping at domains caused by S.R.O. or at sub-microscopic Al precipitates, in a manner similar to that proposed by Barlow (1977).

After a short in-situ anneal at 550°C such foils readily nucleated a high density of Frank loops, which eventually promoted void formation. Indeed some Cu 10% Al foils after an in-situ anneal treatment nucleated voids more rapidly than in pure copper foils. However, the experimental observations of void formation in Cu/Al alloys were only of a qualitative nature and further research is needed in this important area, particularly to classify the loop density, type, dislocation density and subsequent void network.

11.6 Loop Growth Rates

Investigations into the growth rate of loops revealed that while Frank growth can be explained by diffusion equations as proposed by Kiritani (1975), rhombus perfect growth cannot. The apparent activation energy for loop growth in a given metal should be $\triangleq \frac{1}{2} E_v^m$ Urban (1971). Measurements of Frank loop growth in Cu and in annealed Cu 16% Al foils showed that E_v^m for Cu $\triangleq$ .62 eV and E_v^m for Cu 16% Al $\triangleq$ 1.14 eV. Further experiments in Cu .31% Al specimens indicated that the activation energies of Frank and perfect loops in the same specimen were different. This result suggests that while the growth of Frank loops may be diffusion controlled, that of rhombus loops may be controlled by the ease of nucleation of jogs, so that under certain conditions, the growth of perfect loops is jog controlled. Weak beam studies of both types of loops suggests that Frank loops grow by the movement of constrictions along the Shockley stair-rod dislocations, while perfect loops may grow by the movement of extended superjogs.

Accurate measurement of loop growth revealed that while rhombus loops grew linearly at all temperatures, Frank loops developed a series of growth stages. When a steady state is established, linear growth

occurs, but as the sink density and vacancy concentration increases the loop growth rate slowly decreases, with increasing dose.

Experiments on annealed Cu/Al foils revealed that at a given irradiation temperature, as the loop density increased, the time exponent of loop growth decreased from 1 to .5. Further experiments on Frank loop growth in copper revealed that loop growth rates were dependent not only on the position in the foil, but on the proximity of other loops. Computer calculations are at present being carried out by Imeson in order to understand these observations.

11.7 Preferred Loop Orientations

Cu/Al specimens (cut from slowly grown crystals) nucleate on irradiation (without being subject to an in-situ anneal) predominantly perfect loops with an uneven distribution on the various {110} planes. Fig. 11/1(a) shows the relative percentages of three loops which were in contrast in a Cu 16% Al specimen, as a function of irradiation temperature. Loops A and C have 42% and 25% of the loop population counted while loop B contributes the remainder. These proportions remained the same until at $T_i \simeq 210^{\circ}C$ the loops appeared to be equally divided on the planes, though measurements were not statistically significant above $T_i = 220^{\circ}C$, due to the small numbers of loops present.

Fig. 11/1(b) illustrates the effect of thickness on the asymmetry of loop distribution for a Cu 16% Al foil irradiated at $210^{\circ}C$, in which, as the thickness increases, the asymmetry increases. These measurements in the thick foils and at temperatures $< 210^{\circ}C$ were found to be reproducible from one specimen to another. Experimental results were also obtained from foils irradiated along three different beam directions $\bar{z} = [211]$, $\bar{z} = [110]$ and $\bar{z} = [111]$, the details of which are shown on table 10. Also shown is a typical distribution of Frank loops in an annealed Cu 2% Al specimen. The fraction of total loop population

Table 10

$\bar{F}$ = [111] $\bar{z}$ = [211] T_i = 180°C Cu 16% Al

$\bar{g}$ \ $\bar{b}$	011	$10\bar{1}$	$1\bar{1}0$	110	$0\bar{1}1$	101
$1\bar{1}\bar{1}$	29%	24%	46%			
$\bar{1}\bar{1}1$		33%		23%	43%	
$\bar{1}1\bar{1}$			41%		26%	32%
Total % all loops	16%	13%	24%	10%	17%	20%

(A)

$\bar{F}$ = 110 $\bar{z}$ = 110 T_i = 195°C Cu 16% Al

$\bar{b} = \frac{1}{2}[1\bar{1}0]$ 21%

$\bar{b} = \frac{1}{2}[011]$ 17.6%

$\bar{b} = \frac{1}{2}[101]$ $\frac{1}{2}$ $0\bar{1}1$ 16.6%

$\bar{b} = \frac{1}{2}[\bar{1}01]$ 15.2%

$\bar{b} = \frac{1}{2}[110]$ 13%

(B)

$\bar{F} = \bar{z}$ = 111 T_i = 190°C Cu 16% Al

$\bar{b} = \frac{1}{2}[1\bar{1}0]$ 26%

$\bar{b} = \frac{1}{2}[101]$ 24%

$\bar{b} = \frac{1}{2}[0\bar{1}1]$ 17.8%

$\bar{b} = \frac{1}{2}[011]$ 10%

$\bar{b} = \frac{1}{2}[10\bar{1}]$ 13% (Measurements made by Imeson)

$\bar{b} = \frac{1}{2}[110]$ 8.5%

(C)

Cu 2% Al Annealed 5 minutes 550°C Frank loops

$\bar{F}$ = [111] $\bar{z}$ = [211] T_i = 240°C

$b = \frac{1}{3}[111]$ 20%

$\bar{b} = \frac{1}{3}[1\bar{1}\bar{1}]$ 30.3% 974 loops measured

$\bar{b} = \frac{1}{3}[\bar{1}\bar{1}1]$ 22.9%

$\bar{b} = \frac{1}{3}[\bar{1}11]$ 26.8%

(D)

measured on each plane varied from 20% to 30%, while measurements by Okamoto and Harkness (1973) on the Frank loop distribution in a stainless steel foil irradiated at 410°C under a loop stress of 30 K.S.I. revealed an asymmetry on each (111) plane of

34% $(\bar{1}\bar{1}1)$

27% (111)

22% $(\bar{1}11)$

18% $(1\bar{1}1)$

The results are surprising in view of the fact that no deliberate stress was applied to the Cu/Al foils. However, the presence of S.R.O. in conjunction with gases or precipitates may be promoting the observed asymmetry, though this argument could not be invoked to explain the loop distributions in pure copper specimens. One interesting feature of the Frank loop asymmetries measured in stainless steel or Cu 2% Al is that if Frank loops on one plane can produce equal numbers of the three perfect loops that can be derived from them by shear then the following perfect loop distribution can be obtained:-

Cu 2 at.% Al		Stainless Steel (Okamoto)	
$(1\bar{1}0)$	19%	$(1\bar{1}0)$	20.3%
$(10\bar{1})$	18%	(101)	18.6%
(011) $(0\bar{1}1)$	17%	$(0\bar{1}1)$	17.3%
(101)	16%	(011)	16.3%
(110)	14%	$(10\bar{1})$	15.3%
		(110)	13.3%

These distributions are not inconsistent with those experimentally measured.

Okamoto and Harkness (1973) have used their results to support Brailsford and Bullough's (1972) suggestion that stress biased loop nucleation is an important mechanism for radiation enhanced creep in type 316 stainless steel. However, further investigations need to be

made into the causes of such asymmetry especially in copper.

11.8 Other Factors

Further experiments should also be performed

(a) To determine the threshold for damage in Cu/Al alloys.

(b) To investigate the nature of the very small defects which (1) appeared in foils which had been subjected to long anneals in the microscope prior to irradiation and (2) foils which had not been annealed in the microscope, but had been subjected to long periods of irradiation at elevated temperatures.

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