THE EFFECT OF DISPERSED PARTICLES ON THE PRIMARY RECRYSTALLISATION OF ALUMINIUM-ZIRCONIUM ALLOYS.

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by

G.A. FITZPATRICK, B.Sc.(Hons.), GRAD.I.M.

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The isothermal and isochronal recrystallisation characteristics of a series of aluminium-zirconium dispersion alloys have been investigated as a function of the particle size, the interparticle spacing, the matrix grain-size and the amount of prior cold-deformation. The investigation was based on the use of hardness measurements and metallographic examinations at various stages of the recrystallisation process. Particle characteristics were determined by quantitative metallography techniques.

Recrystallisation was accelerated as the particle size increased (for approximately similar centre-to-centre nearest neighbour spacings), or as the number of particles increased (for similar particle sizes) when the dispersion consisted of widely spaced coarse particles (for centre-to-centre nearest neighbour distances in the range 7 to 15 microns). This particle-accelerated recrystallisation was found to be associated with an increased nucleation rate, a relatively unchanged growth rate, and a decreased sensitivity to changes in the matrix grain-size as the particle content increased (i.e. as the interparticle spacing decreased).

In the case of finer dispersions it was found that recrystallisation was severely retarded as the interparticle spacing was decreased below approximately 3 microns. In particular, an alloy containing fine particles, at a centre-to-centre nearest neighbour distance of 1.75 microns, was not fully recrystallised after having been held at 375°C for a week following a room temperature rolling reduction of 60% in thickness. This retardation of recrystallisation was found to be associated with marked reductions in both the nucleation and growth rates of the recrystallising grains.

It was found that the final recrystallised grain-size of the alloys decreased as the particle content increased in the acceleration region, but increased as the particle content increased in the retardation region. The finest grain-size was, therefore, produced in an alloy for which the recrystallisation rate was the most rapid. The results are shown to be consistent with the Mould-Cotterill hypothesis for the recrystallisation of dispersion alloys.
1. LITERATURE SURVEY.

1.1. INTRODUCTION AND CLASSIFICATION OF PHENOMENA.

1.2. THE STRUCTURE OF DEFORMED METALS.

1.2.1. Work-hardening.

1.2.2. Microstructure.
   1.2.2.1. Examination by X-ray techniques.
   1.2.2.2. Examination by transmission electron microscopy.

1.2.3. The internal energy of deformed metals.
   1.2.3.1. Structural aspects.
   1.2.3.2. Experimental aspects.

1.2.4. Factors affecting the structure of deformed metals.
   1.2.4.1. Stacking-fault energy.
   1.2.4.2. Solute atoms.
   1.2.4.3. Second-phase particles.
   1.2.4.4. Grain-size.

1.3. RECOVERY.

1.3.1. Recovery of microstructure.

1.3.2. Recovery of stored internal energy.

1.3.3. Recovery of mechanical properties.

1.3.4. Factors affecting recovery.

1.3.5. The influence of recovery on the driving force for primary recrystallisation.
1.4.1. General characteristics.

1.4.1.1. Laws of recrystallisation.

1.4.1.2. Comparison of the techniques available for the assessment of recrystallisation.

1.4.2. The nucleation of grains during primary recrystallisation.

1.4.2.1. General aspects.

1.4.2.2. The classical nucleation model.

1.4.2.3. Preformed nucleus models.
   1.4.2.3.1. Block theories of nucleation.
   1.4.2.3.2. Polygonisation and cell-growth theories.
   1.4.2.3.3. Sub-grain coalescence by rotation model.
   1.4.2.3.4. Geometric coalescence model.
   1.4.2.3.5. Comparison of preformed nucleus models.

1.4.2.4. Martensitic nucleation model.

1.4.2.5. Bulge nucleation model.

1.4.3. The growth stage of primary recrystallisation.

1.4.4. The kinetics of primary recrystallisation.

1.4.5. General factors which influence recrystallisation.

1.4.5.1. The amount of prior deformation.

1.4.5.2. The original grain-size.

1.4.6. Primary recrystallisation in solid-solution alloys.

1.4.6.1. Experimental observations.

1.4.6.2. Theoretical interpretations.
   1.4.6.2.1. General aspects.
   1.4.6.2.2. Solute-dependent nucleation.
   1.4.6.2.3. Solute-dependent growth.
      1.4.6.2.3.1. The Lücke and Detert theory of impurity -dependent grain-boundary migration.
      1.4.6.2.3.2. Modifications to the Lücke-Detert model
      1.4.6.2.3.3. Other theories of solute-dependent growth.

1.4.7. Primary recrystallisation in two-phase alloys.

1.4.7.1. General aspects.

1.4.7.2. Accelerated recrystallisation.
1.4.7.4. Retardation of grain boundary migration by a fine dispersed phase.

1.5. GRAIN GROWTH. ... 67

1.6. SUMMARY. ... 69

1.7. THE PRESENT WORK. ... 70

1.7.1. Objectives.

1.7.2. Selection of alloy system.

1.7.3. The characteristics of the aluminium-zirconium system

2. EXPERIMENTAL TECHNIQUES. ... 76

2.1. INTRODUCTION. ... 76

2.2. SPECIMEN PREPARATION. ... 78

2.2.1. Materials.

2.2.2. Casting.

2.2.2.1. Alloys with a two-phase as-cast structure.

2.2.2.2. Alloys with a super-saturated solid-solution structure.

2.2.3. Production of homogeneous dispersions.

2.2.3.1. Forging of two-phase alloys.

2.2.3.2. Precipitation from super-saturated solid-solution alloys.

2.2.4. Standardisation of matrix phase.

2.2.4.1. Solute content.

2.2.4.2. Grain-size.
2.3. SPECIMEN ASSESSMENT.

2.3.1. Constitution.
   2.3.1.1. Composition.
   2.3.1.2. Phase analysis.

2.3.2. Metallography.
   2.3.2.1. Specimen preparation
      2.3.2.1.1. Optical microscopy.
      2.3.2.1.2. Electron (stereoscan) microscopy.
   2.3.2.2. Quantitative metallography.
      2.3.2.2.1. Matrix grain-size.
      2.3.2.2.2. Particle shape.
      2.3.2.2.3. Particle distribution.
      2.3.2.2.4. Particle size.
      2.3.2.2.5. Particle volume fraction.
      2.3.2.2.6. Inter-particle spacings.

2.4. STUDY OF RECRYSTALLISATION CHARACTERISTICS. ... 88

2.4.1. Deformation.

2.4.2. Annealing.
   2.4.2.1. Isochronal annealing.
   2.4.2.2. Isothermal annealing.

2.4.3. Assessment of recrystallisation.
   2.4.3.1. Macrohardness measurements.
   2.4.3.2. Metallography.

3. RESULTS. ... 92

3.1. ALLOY CHARACTERISTICS. ... 92

3.1.1. Composition.

3.1.2. Phase identification.

3.1.3. Dispersion data.
3.2. DEFORMATION AND ANNEALING CHARACTERISTICS. ... 93

3.2.1. Deformation.

3.2.2. Isochronal annealing.
   3.2.2.1. The effect of zirconium in solid-solution.
   3.2.2.2. The effect of the matrix grain-size in two-phase alloys.
   3.2.2.3. The effect of the amount of prior deformation in two-phase alloys.

3.2.3. Isothermal annealing at 335°C.
   3.2.3.1. The effect of zirconium in solid-solution.
   3.2.3.2. The effect of the matrix grain-size in two-phase alloys.
   3.2.3.3. The effect of the amount of prior deformation in two-phase alloys.

3.2.4. Isothermal annealing at 375°C.

3.2.5. The effect of annealing temperature and time on the behaviour of two-phase alloys having similar initial grain-sizes.

4. DISCUSSION. ... 159

4.1. THE PRESENT RESULTS. ... 159

4.1.1. Comparison of the formulae available for the evaluation of inter-particle spacing.

4.1.2. The annealing of solid-solution alloys.

4.1.3. The isochronal annealing of two-phase alloys.
   4.1.3.1. The effect of the matrix grain-size.
   4.1.3.2. The effect of the prior deformation.
   4.1.3.3. The effect of particle size and concentration.
4.1.4. Recrystallisation kinetics in two-phase alloys.

4.1.4.1. The effect of grain-size.

4.1.4.2. The effect of prior deformation.

4.1.4.3. The effect of particle concentration.

4.1.4.4. The effect of annealing temperature.

4.2. THE MECHANISM OF RECRYSTALLISATION IN TWO-PHASE ALLOYS.

4.2.1. The Mould-Cotterill hypothesis.

4.2.2. The present investigation.

4.2.3. Summary.

5. CONCLUSIONS.

6. RECOMMENDATIONS FOR FURTHER WORK.

7. REFERENCES.

8. ACKNOWLEDGEMENTS.

APPENDIX.
1. Introduction and classification of phenomena.

It has been known since prehistoric times that metals can be softened by heating. But, it was not until 1926 that recrystallisation was recognised as a nucleation and growth process by which a stable nucleus is first formed and then grows through the deformed material (1). Since then, a considerable quantity of investigations has been carried out and several reviews (2-5) on the subject have been written. The development of high-resolution microscopy techniques in recent years has provided detailed evidence of the structure of deformed metals and of the changes it undergoes during annealing.

The structural damage produced when a metal is cold-worked leads to a substantial strain energy stored in the lattice. Such a condition is thermodynamically unstable relative to the undeformed state. The deformed metal, therefore, tries to revert to a state of decreased internal energy. This cannot occur spontaneously but only at elevated temperatures where the thermally activated structure-repairing mechanisms can take place. The structure is renovated by a combination of three processes: recovery; recrystallisation; and grain growth. The driving force for both recovery and recrystallisation is provided by the high internal energy of the deformed metal while that for grain growth is provided by the interfacial energy of the grain boundaries in the recrystallised state.

The following classification of the processes involved is based on that given by Cahn (6).

**Recovery** applies to all those changes which do not involve the migration of high angle boundaries throughout the whole of the deformed structure. The deformed crystal (or polycrystalline aggregate), therefore, retains its basic identity, although the density and distribution of internal defects change.

**Recrystallisation** applies to those stages in which the crystal orientation of any region in the deformed metal is altered, maybe more than once, by the passage of high angle grain boundaries through the material.

In **primary recrystallisation**, new grains are first nucleated and then grow at the expense of the deformed material until it has all been consumed. This stage is then complete and the metal has a minimum recrystallised grain
Grain growth involves the further migration of grain boundaries at a reduced rate throughout the structure.

In normal grain growth, all boundaries migrate at approximately equal rates to produce a roughly uniform grain size at any instant. The final structure consists of a smaller number of grains, the average size of which is larger than at the end of primary recrystallisation.

Grain growth is occasionally restricted to a small number of boundaries so that a few grains become very large at the expense of the rest. This production of a coarse non-uniform structure is termed secondary recrystallisation (or abnormal grain growth).

The term recovery is also often applied to the gradual return of physical and mechanical properties to values characteristic of the undeformed state, irrespective of the mechanism by which this change is brought about. The reference state is always the completely recrystallised condition.
1.2. The structure of deformed metals.

1.2.1. Work-hardening.

The properties of a metal are altered when it is deformed at temperatures which are low relative to its melting point i.e. yield strength, tensile strength, hardness and electrical resistivity increase; the ductility and density decrease. The changes in mechanical properties are of particular importance in industrial practice as the rate at which a metal hardens during cold-work influences both the power required and the method of deformation in the shaping operations, while the extent of the hardness governs the frequency of annealing operations to enable further working of the metal.

The multiplication of dislocations during plastic deformation increases the stress necessary for dislocation motion. The magnitude of hardening depends sensitively on the distribution of dislocations. Taylor (7) proposed that some dislocations become lodged in the lattice and act as sources of internal stress which oppose the motion of other dislocations. All subsequent theories of work-hardening are based on this hypothesis, differing only in the manner in which dislocations interact to cause the reduction in mobility.

The stress-strain curve typical of a F.C.C. single crystal is shown in Figure 1. Three regions of hardening are experimentally distinguishable.

Stage I, or the easy glide region, is characterised by a low rate of work-hardening immediately after the yield point. The extent of this region is dependent on the orientation and purity of the crystal, the temperature and the specimen dimensions.

Stage II, or the linear hardening region, shows a rapid increase in work-hardening at an approximately constant rate which is independent of the above factors.

Stage III, or the parabolic hardening region, exhibits a low rate of work-hardening. The start of this region is strongly temperature dependent.

Stage I occurs in crystals oriented for glide in a single slip system. The dislocations mainly glide out of the crystal at the free surface, as indicated by the slip-line pattern which is of fine slip with very long slip lines comparable with the diameter of the specimen.
Stage II is characterised by the occurrence of slip on secondary as well as primary slip systems. Several new lattice irregularities may then be formed, including forest dislocations, Lomer-Cottrell barriers and jogs. Each of these forms the basis of separate mechanisms for Stage II hardening in which the flow stress is controlled either by long-range stresses from piled-up groups of dislocations (8), or by sessile jogs on gliding dislocations (9), or by the bowing-out of lengths of dislocation in the network (10). The hardening rate depends on the arrangements of dislocations assumed. Smallman (11) suggested that none of the proposed mechanisms is able to explain satisfactorily all the experimental observations, and that a composite theory combining suitable segments of the individual mechanisms may be more successful. The length of slip-lines decreases during Stage II.

During Stage III, the rate of work-hardening is lower than in Stage II, mainly because screw dislocations can cross-slip, and therefore by-pass, the obstacles that hindered dislocation motion in the previous stage. This leads to a substantial increase in the length of slip-lines, which are interconnected with short cross-slip lines.

Metals with a cubic structure are capable of deforming in a complex manner on more than one slip system, resulting in the behaviour outlined above for single crystals. For polycrystalline specimens, only Stage III behaviour occurs from the beginning of deformation. Such metals normally show a strong work-hardening behaviour. Metals with a hexagonal structure slip only on those planes parallel to the basal plane at low temperatures. They have single crystal stress-strain curves similar to Stage I for F.C.C. single crystals, and have a low rate of work-hardening. In polycrystalline hexagonal specimens, plastic deformation is much more complicated and additional deformation mechanisms, such as twinning, operate.

1.2.2. Microstructure.

1.2.2.1. Examination by X-ray techniques.

Gay, Hirsch and Kelly (12) used a micro-beam Debye-Scherrer X-ray technique to examine the sub-structure of deformed metals. They concluded that dislocations lie mainly in boundaries which occupy about one-half the
total volume in copper and one-fifth in aluminium. Honeycombe et al. (13) applied the Berg-Barret technique to aluminium, and found lattice rotations in regions separated by kink bands together with lattice misorientations parallel to the primary glide plane. This type of structure is found soon after the end of Stage I.

Kink bands have been examined by measuring the asterism of Laue spots. A small but measurable amount of asterism occurs in Stage I (13). The extent of the asterism increases slowly in Stage II, and very rapidly in Stage III. The nature of the lattice rotations leading to asterism are poorly understood.

1.2.2.2. Examination by transmission electron microscopy.

Thin-film electron microscopy has been used to study specific dislocation reactions in work-hardened single crystals, and the sub-structure formed when polycrystalline specimens are deformed. However, this technique, although attractive, has two major criticisms. Firstly, the size of specimens which can be examined makes it impossible for any one micrograph to be typical of the dislocation arrangement within a large bulk of material. Secondly, dislocations may be lost from the foil either during its preparation or later.

Heidenreich (14), using electron microscopy, showed that the regions inside the grains of deformed high-purity aluminium are broken up into an arrangement of slightly misoriented cells. The first detailed description of a cell structure was given by Gay et al. (12) (Section 1.2.2.1).

Very low amounts of deformation produce random slip-line traces on the thin-foil micrograph. But increasing the deformation produces a larger number of dislocations and a cell structure forms. The following summary of the main features of the cell structure in F.C.C. metals is due to Swann (15):

(i) The cell size is independent of the initial grain size and decreases to a limiting value after a certain strain. (Figure 2).

(ii) The limiting value of the cell size increases with the softness of the metal.

(iii) The width of the cell walls increases with the hardness of the metal.
Fig. 1. Schematic stress-strain curve of a FCC single crystal showing the three stages of work-hardening.

Fig. 2. Cell-size of aluminium as a function of deformation.

Fig. 3. Cell-size of iron as a function of deformation.
The cell interiors are relatively free from dislocations, whereas the walls are regions of high dislocation density. There is a general tendency for cell walls to lie parallel to low index planes in F.C.C. metals i.e. alignment is common along \{100\}, \{110\} and \{111\} planes in aluminium (15). It also seems to be a general rule that a small cell size is associated with more ragged cell walls. Weissmann et al. (16) observed that the misorientation across cell walls in aluminium was small when the cell structure was first formed, but that the walls became more delineated as the deformation increased. Bailey, however, reported that misorientations in silver (17) and copper (18) were too small to be detected by diffraction techniques, and they were, therefore, taken as less than 2°.

Keh and Weissmann (19) reviewed the formation of cell structures in B.C.C. metals, and reached similar conclusions to those of Swann for F.C.C. metals. As with F.C.C. metals, when the cell structure has formed, further deformation causes a decrease in cell size to a limiting value of about 2 microns (Figure 3).

The lack of study of the deformation sub-structure of polycrystalline CPH metals by this technique is due to the tendency for recovery to occur during the thinning of specimens at room temperature. Other factors are the large amounts of deformation which can occur by basal glide, and the occurrence of an alternate deformation mechanism, twinning.

1.2.3. The internal energy of deformed metals.

1.2.3.1. Structural aspects.

When a metal is cold-worked, most of the energy appears as heat, but a small fraction is stored within the metal as strain energy. It is this stored energy of cold-work which provides the driving force for recovery and recrystallisation, and it is associated with the increased number of dislocations, stacking faults, and point defects. The amount of energy retained depends on the deformation process, the deformation temperature and the composition of the metal (20). Figure 4 indicates that the stored energy of cold-work increases with increasing deformation but at a decreasing rate.
The dislocation density of metals increases from values such as $10^6 - 10^8$ dislocations/cm$^2$ for annealed metals to $10^{10} - 10^{12}$ dislocations/cm$^2$ for heavily deformed metals. During the rapid hardening of both single crystal and polycrystalline specimens, the dislocation density is related to the applied stress as follows (17-19):

$$\sigma = a \mu b \rho^{1/2} \ldots (1)$$

where $\sigma$ = applied stress
$a$ = content (0.2 - 0.3)
$\mu$ = shear modulus
$b$ = Burger's vector
$\rho$ = dislocation density

Nabarro et al. (21) have reviewed the theoretical models proposed for this relationship. An important difference between the behaviour of polycrystalline and single crystal specimens is the observation that the dislocation density of the former reaches a limiting value, whereas that of the latter does not (22).

Seitz (23) has shown that an increased vacancy concentration due to deformation contributes to the total stored energy in a metal. The effect, however, of the formation of interstitial atoms on stored energy is unknown, although it can be assumed that vacancies with less associated strain energy will be found in greater numbers than interstitial atoms during cold-working.

The formation of stacking-faults during deformation can contribute greatly to the total stored energy, especially in those metals which have a low stacking-fault energy. (See section 1.2.4.1).

### 1.2.3.2. Experimental aspects.

The stored energy of deformed metals has been measured by the following main techniques:

(i) measurements of the difference between the heat evolved during deformation and the work done on the specimen;

(ii) differential calorimetry, i.e. the difference in power supplied to heat a deformed and a fully annealed specimen is measured; and

(iii) solution calorimetry, in which the heat of solution on dissolving deformed and undeformed specimens is compared.

A review of experimental data has been made by Titchener and Bever (45).
The use of these techniques has enabled the following conclusions to be made about the stored energy of deformed metals:

(i) The absolute value of the stored energy increases as the strain increases. For polycrystalline aluminium and copper, it reaches a limiting value, whereas for single crystal specimens it does not. (22).

(ii) The proportion of the total energy which is stored decreases as the strain increases.

(iii) The amount of stored energy increases as the melting point of the metal increases.

The attainment of a limiting stored energy value, at high strains, in polycrystalline specimens is associated with the restriction to dislocation movement imposed by grain boundaries (24). Dislocation density measurements also show a limiting value in polycrystalline specimens (24). In single crystals, dislocation multiplication leads to high energy configurations on a small number of planes.

1.2.4. Factors affecting the structure of deformed metals.

1.2.4.1. The stacking-fault energy.

A stacking-fault within a metal crystal is bounded by partial dislocations (25). The width of the fault is inversely proportional to the stacking-fault energy of the metal. Metals such as copper, with low stacking-fault energy values, produce wide stacking-fault ribbons, making cross-slip difficult during deformation. In metals with high stacking-fault energy values, such as aluminium, cross-slip can occur at room temperature. The general structure of a cold-worked metal is, therefore, influenced by its stacking-fault energy.

The dislocation density of a deformed metal increases as the stacking-fault energy increases at constant strain (26). Also, the stored energy increases as the stacking-fault energy decreases for a wide range of metals (26).

The sharpness of the cell walls formed during deformation varies from metal to metal in a way which correlates with the stacking-fault energy. Hirsch (27) has inferred that a cell structure results from the ability of screw
dislocations to cross-slip out of their original slip planes and arrange themselves into very localised regions which form the walls of relatively strain-free cells. Well-defined cell structures are consequently found in metals with high stacking-fault energy values (e.g. Al, Ni, Fe).

1.2.4.2. Solute atoms.

Gay et al. (12, 28) were the first to report that solid-solution elements reduce the cell size in deformed metals. Investigations on silver and nickel solid-solution alloys (29) concluded that increasing the solute content leads to a decrease in the stacking-fault energy, which in turn influences the cell size. Swann (15) regards the stacking-fault energy as the principal factor determining the dislocation density in such alloys.

The behaviour of solid-solution alloys based on solvents with a high stacking-fault energy is less clearly understood. The low solubility of most elements in aluminium alloys at room temperature is such that it is necessary to quench from elevated temperatures to retain a range of solid-solution compositions. This introduces large numbers of defects (e.g. vacancies) into the structure with the consequent formation of dislocation loops which interfere with the normal processes of cell formation (30). The strain required to form a cell structure in a quenched material is greater than in a slowly cooled one, since the mobile dislocations interact with vacancies to produce jogs. These, in turn, reduce the mobility and slip distances of the dislocations (31).

BCC metals are usually considered to have high stacking-fault energy values, and they normally exhibit a well-defined structure in the deformed condition. However, the addition of 3% silicon to pure iron lowers its stacking-fault energy by about four-fifths, the dislocation distribution alters, and the cell size becomes smaller and less well-defined (32).

The general rule seems to be that increasing the solute content of an alloy increases the dislocation density and stored energy for any given state of strain, regardless of lattice type and/or stacking-fault energy. Examples have been quoted in aluminium (15), iron (19, 32) and nickel (33).
1.2.4.3. Second-phase particles.

When a finely-divided second-phase is distributed in a metallic matrix, an alloy is formed which is considerably stronger than the matrix itself. Several mechanisms for the increased work-hardening capacity of such alloys have been postulated (34-36), and it is evident that dispersed particles exert a major influence on the nature of the cold-worked structure.

The size and spacing of dispersed particles determine the extent of their effect on dislocation distribution after cold-work. In precipitation alloy systems, the nature of the matrix and/or particles appears to be of minor importance provided the interface is incoherent. The important parameter appears to be the particle size. Swann (15) has shown that, in aluminium-copper alloys, coarse, widely-spaced particles promote the formation of a cell structure since they act as dislocation sources and determine the position of the cell walls. Fine particles (< 1 micron diameter), however, appear to inhibit cell structure formation during deformation. In this case, the deformation required to initiate a cell structure is greater, and the cell size is smaller for any given strain, than in the corresponding single phase metal. Also, the dislocation density is increased, compared with the single phase metal, and a larger proportion of dislocations are situated inside the cells instead of the cell walls. As the deformation increases, the distinction between cell-interiors and cell walls becomes less clear, and the concept of a cell-structure does not apply. This effect has been found in many systems, including Cu-Co (37), Al-Al₂O₃ (38) and Cu-Al₂O₃ (39).

Barton and Ansell (40) investigated the behaviour of aluminium-silver alloys under conditions in which the particle/matrix interface was coherent. In their specimens, the precipitate was present as platelets within which a sub-structure was visible after deformation.

Sundberg et al. (143) reported that the deformation sub-structure in their Al-Zr alloys varies with the precipitation structure. Between the fan-shaped arrangements of precipitates, they found fine, well-developed sub-grains. A high, homogeneous dislocation density but no sub-grain formation was found where the fan-branches lay densely. When the precipitate arms are widely separated, sub-grains form between them. In areas with small
precipitates, they observed the pinning of sub-grains and dislocations by the particles.

1.2.4.4. Grain-size.

In iron (19) and copper (41), the dislocation density after deformation has been found to be greater for fine-grained specimens than for coarse ones. An explanation for the variation of dislocation density with grain-size is given by Conrad and Christ (43) in terms of the average distance moved by dislocations. Interpreting the results on iron, they found that

\[ S = k_1 \cdot d^n \] \hspace{1cm} \text{...(2)}

and \[ e = \alpha \rho \cdot b \] \hspace{1cm} \text{...(3)}

where \( S \) = average distance moved by dislocations during deformation;
\( k_1 \) and \( n \) = constants varying with strain;
\( d \) = grain size;
\( b \) = Burger's vector;
\( e \) = strain;
\( \rho \) = dislocation density;
\( \alpha \) = constant relating tensile strain to shear strain.

Combining (2) and (3), they obtained an expression relating dislocation density and grain-size, as follows:

\[ \rho = \frac{e}{a k_1 b} \cdot \frac{1}{d^n} \] \hspace{1cm} \text{...(4)}

Their values are plotted in Figure 5, where it is apparent that the dislocation density becomes less sensitive to changes in grain-size as the strain increases.

It has also been found that the stored energy of deformed metals increases as the grain-size decreases (44, 45). Conrad and Christ (43) examined the results of Clarebrough et al. (41) for copper and derived the following equation relating grain-size and stored energy:

\[ E = \frac{e}{k_2 b} \cdot \frac{1}{d^n} \] \hspace{1cm} \text{...(5)}

where \( E \) = stored energy released during primary recrystallisation
\( k_2 \) = constant relating stored energy to dislocation density.
Their results are shown in Figure 6.

Despite its effects on dislocation density and stored energy, it has been reported that the cell size of deformed metals does not vary with the initial grain-size (12, 28, 41).
Fig. 4. Stored energy of cold-work and fraction of total work of deformation remaining as stored energy for copper as functions of tensile elongation.

Fig. 5. Dislocation density as a function of grain-size for iron deformed at room temperature.

Fig. 6. Stored energy as a function of grain-size for copper compressed various amounts.
1.3. Recovery.

1.3.1. Recovery of microstructure.

Cahn (46, 47) studied the effects of annealing bent single crystals of zinc, aluminium, magnesium and sodium chloride. By using the Laue method of X-ray diffraction, he observed the formation of small-angle sub-grain boundaries which separate strain-free sub-grains. He termed this polygonisation. Reflections from the bent single crystals took the form of continuous asterated spots. On annealing, these asterisms disintegrated into a series of discrete spots, each of which originates from a perfectly polygonised sub-grain. Cahn proposed that the basic movement in the process is one of climb, by which the excess dislocations causing lattice curvature during bending re-arrange themselves into walls or tilt-boundaries normal to the Burger's vector. This is illustrated in Figure 7. The tilt-boundaries have a lower overall strain-energy than the more random dislocation arrangement formed during bending. This reduction in strain-energy provides the driving force for polygonisation.

When all the dislocations have aligned themselves into tilt-boundaries, polygonisation continues by the progressive merging of two or more sub-boundaries to form a single tilt-boundary. The driving force for this is derived from the progressive reduction of the boundary area per dislocation within the boundary as the number of dislocations within the boundary increases.

Since it involves dislocation climb, which depends on the migration of vacancies, relatively high temperatures are required for a rapid rate of polygonisation. At lower temperatures, other processes which lower the lattice strain energy are of greater importance. These are considered to be a matter of reducing the number of point defects to their equilibrium value (6).

It has been discussed in section 1.2.2.2, that the dislocations produced during plastic deformation are already partially arranged in sub-boundaries giving diffuse cell structures, the sharpness of the cell structure depending on the stacking-fault energy of the metal. During subsequent recovery treatments, these cell-walls sharpen, and the cells grow larger as their interiors are depleted of dislocations. The mechanism by which the cell-walls sharpen and grow is a complex form of polygonisation (6).
are present on several slip planes, the cell-walls cannot be simple tilt-boundaries. They are, however, very similar as both cell-walls and tilt-boundaries appear in the form of rows of etch pits on an etched section (48). The dislocations can reduce the stored energy by mechanisms such as mutual annihilation or alignment into regular arrays. Polygonisation of edge dislocations takes place by climb, and screw dislocations form sub-boundaries by thermally-activated cross-slip. The growth of some sub-grains at the expense of others is analogous to the growth of polygonised sub-grains by the merging of pairs of tilt-boundaries. Adjacent sub-boundaries merge because the boundary energy per dislocation in the boundary decreases with increasing angle of misorientation. Unlike simple tilt-boundaries, these boundaries increase in mobility with increasing misorientation. Sub-grain growth has also been observed to occur by coalescence of neighbouring grains by a process of climb and sub-grain rotation (49). Both the merging of sub-boundaries and sub-grain coalescence may be important in the nucleation of a recrystallised grain. (See section 1.4.2.3.)

The basic differences between the formation of a sub-structure by polygonisation and the cell structure formed during cold-work have been summarised by Byrne (50), as follows:

(a) In polygonisation, an excess of one type of dislocation is required.
(b) Polygonisation is not produced directly during low temperature cold-work, whereas sub-grains do originate during cold-work.
(c) Polygonisation requires either an elevated temperature anneal, or concurrent creep, or deformation at an elevated temperature; deformation sub-grain formation does not.
(d) The size of the polygonised sub-structure is often an order of magnitude larger than that of a typical sub-grain formed during cold-work.

1.3.2. Recovery of stored internal energy.

Although the changes involved in recovery and recrystallisation differ considerably, the driving force in each case is the reduction of the high internal energy of the deformed condition. On annealing, the stored energy due to cold-work is released as heat, which can be measured in very sensitive
Fig. 7. Arrangement of excess dislocations in a bent crystal (a) before and (b) after polygonisation.

Fig. 8. Heat evolution curves for copper deformed to 30% elongation.

Fig. 9. Rate of release of stored energy, electrical resistivity and hardness as functions of temperature for nickel deformed in torsion and heated at 60K/min.
differential calorimeters by comparing the specific heats of a deformed and undeformed sample.

Gordon (20) studied the isothermal annealing of high-purity copper, previously deformed in tension at room temperature. Typical curves are shown in Figure 8. The energy is released in two stages, the first being associated with recovery, the second with recrystallisation. Similar effects have been reported for high-purity silver (17).

Clarebrough et al. (51, 52) determined the stages of stored energy release for both copper and nickel. Figures 9 and 10 correlate the energy release with the changes in other physical properties. For nickel, there are three fairly precise stages, the first two being associated with recovery, and the last with recrystallisation. For copper, the energy release due to recovery is either absent or spread over a long temperature range.

In general, it is thought that the energy released during recovery is associated with the annihilation of vacancies and the re-arrangement of dislocations, with or without the formation of a cell structure (54).

1.3.3. Recovery of mechanical properties.

Metals can be divided into two general groups in terms of changes in their mechanical properties during recovery. Metals with a low stacking-fault energy value usually show very little change in such properties for the reasons outlined in section 1.2.4.1. In metals with a high stacking-fault energy value, dislocation re-arrangement can occur quite easily within the deformed metal if the temperature is high enough. Such metals can soften considerably during a low temperature anneal. Under favourable circumstances, the whole of the work-hardening can be recovered without recrystallisation occurring. The general rule is that the larger the deformation, the smaller is the fraction of recoverable work-hardening prior to recrystallisation. (6).

1.3.4. Factors which affect recovery.

Most of the factors which influence the cold-worked structure will also have an effect on either the degree of recovery of physical properties or the temperature at which recovery occurs.
The effect of stacking-fault energy on recovery has been discussed by McLean (55) and outlined in section 1.3.3. High stacking-fault energy metals can undergo considerable pre-recrystallisation softening under certain conditions.

Clarebrough et al. (51) have observed that, for 99.6% pure nickel, the proportion of stored energy released on recrystallisation increases as the strain increases. McLean (55) has combined the effects of stacking-fault energy and deformation on recovery as illustrated in Figure 11. In the high stacking-fault energy metal, recovery only precedes recrystallisation at low strains. However, recrystallisation always occurs before recovery in metals with a low stacking-fault energy value.

The effect of metal purity on recovery is minor. There is little recovery in low stacking-fault energy metals whatever the purity. For metals with a high stacking-fault energy, the value is decreased by solutes, but the trend is too small to cause a significant shift in the position of the curves in Figure 11. The effect of increasing the purity could be to move the recovery curve to the left to a greater extent than the recrystallisation curve.

Clarebrough et al. (44) investigated the variation of stored energy with strain for copper with grain-sizes of 0.15 mm and 0.03 mm. They found that both the total stored energy and the manner in which it was released depend on grain size. For strains up to 38%, more energy is stored in the fine-grained metal. For strains of 50% and 70%, the total stored energy is the same for both grain-sizes. The stored energy is released more rapidly for the fine-grained metal. Although the stored energy is independent of grain-size, they found that the recrystallisation temperature is always lower in the fine-grained material. They suggested that the segregation of impurities at the grain-boundaries in the coarse-grained material could account for the anomalous recrystallisation behaviour at high strains. Similar results have been obtained by Loretto and White (57) for a higher-purity copper of grain-sizes 0.15 mm and 0.70 mm.

Titchener and Bever (45) found no influence of grain-size on stored energy for a silver-gold alloy after large deformations. This is also consistent with the results of Clarebrough et al. (44).
1.3.5. The influence of recovery on the driving force for primary recrystallisation.

Vandermeer and Gordon (53), studying the stored energy release in zone-refined aluminium, and Mould and Cotterill (58), who studied the isochronal annealing of super-purity aluminium by micro-hardness distribution measurements, concluded that recovery continues until the whole structure has been consumed by the advancement of recrystallising grains. Figure 12 illustrates schematically the overlapping of recovery and recrystallisation.

Vandermeer and Gordon also carried out experiments to separate the two types of energy release due to recovery and recrystallisation. They clearly found that the occurrence of recovery decreases the driving force for subsequent recrystallisation. In those cases where recovery and recrystallisation occur simultaneously, the driving force for recrystallisation decreases continuously. This arises because the stored energy of unrecrystallised regions decreases progressively due to the continuation of recovery processes. Therefore, the amount of stored energy left to provide a driving force for recrystallisation decreases.
Fig. 10. Rate of release of stored energy, electrical resistivity and hardness as functions of temperature for arsenical copper deformed in torsion.

Fig. 11. Effect of degree of deformation on recovery and recrystallisation of a metal with a high stacking-fault energy (A) and one with a low one (B).

Fig. 12. Overlapping of recovery and recrystallisation.
1.4. Primary recrystallisation.

1.4.1. General characteristics.

1.4.1.1. Laws of recrystallisation.

A large quantity of experimental observations has been summarised into six basic "laws of recrystallisation" by Burke and Turnbull (4).

(a) A minimum deformation is necessary to initiate recrystallisation.
(b) The smaller the amount of deformation, the higher is the temperature required to initiate recrystallisation.
(c) Increasing the annealing time decreases the temperature required for recrystallisation.
(d) The final recrystallised grain-size is generally smaller the greater the degree of deformation or the lower the annealing temperature above that required for recrystallisation.
(e) The larger the original grain-size, the greater is the amount of deformation that is needed for equivalent recrystallisation temperature and time.
(f) The amount of cold-work required to give equivalent hardening increases with increasing temperature of working.

1.4.1.2. Comparison of the techniques available for the assessment of recrystallisation.

The annealing treatments used to study recrystallisation are of two types. Isothermal annealing is used mainly as a source of data which can be manipulated to describe the nucleation and growth rates of the process. Isochronal annealing is used to obtain information of a more technological nature in terms of the temperature range over which recrystallisation occurs.

The conventional techniques used for the study of changes in the recrystallisation process can be compared from the point of view of sensitivity, accuracy, reproducibility of results, and the speed and ease of application.

The micro-hardness population count method is a statistical plot of micro-hardness values taken over the entire surface of a specimen. For partially recrystallised single-phase materials, two distinct frequency peaks
are observed, one representing the cold-worked hardness and the other the fully recrystallised hardness. The extent of recrystallisation is deduced from the relative heights of the peaks. However, this method is not suitable for the evaluation of two-phase materials. The presence of second-phase particles leads to a very wide scatter of micro-hardness measurements and prevents the separation of the results into two distinct peaks in partially recrystallised materials.

X-ray methods have been used in many recrystallisation studies (e.g. 125). They are sensitive in detecting the start of recrystallisation, but accuracy and reproducibility are poor when determining the extent of recrystallisation. The completion of the process is also very difficult to determine by this technique.

The use of the various forms of electron microscopy has revealed a great deal of new information about the nucleation stage of recrystallisation. (See section 1.4.2).

The techniques of electrical resistivity measurements (e.g. 54), calorimetry (e.g. 54) and internal friction (e.g. 59) are difficult to standardise, and, consequently, their use in assessing recrystallisation data has been limited.

Macro-hardness testing is the most commonly applied method in recrystallisation studies because of its procedural simplicity. With care taken over specimen preparation and indentation measurement, accurate and reproducible results can be obtained. An attractive feature of macro-hardness testing is that it measures an average response of the examined region.

Optical microscopy allows the metallographic observation of the extent of recrystallisation and the sites at which the process begins. The success of this technique is governed by the ease with which recrystallised and un-recrystallised regions can be distinguished.

Different values for the temperature (isochronal) or the time (isothermal) at which recrystallisation starts or finishes are often given by hardness measurements and optical metallography. Recrystallisation may be well advanced before the proportion of new grains is sufficient to reduce the overall hardness value.
Towards the end of recrystallisation, hardness measurements can indicate that the process has ended while metallography indicates that, in fact, there are still small regions of unrecrystallised grains. Metallography, therefore, is a more sensitive technique than hardness testing for the detection of the onset or completion of recrystallisation.

For those alloys which undergo extensive recovery softening (prior to recrystallisation), 50% softening occurs much earlier than 50% recrystallisation. Mould and Cotterill (124) have devised a technique which eliminates the influence of pre-recrystallisation softening in the analysis of macro-hardness data. This is accomplished by measuring the slope of tangents to the hardness-temperature curves (for isochronal annealing) or the hardness-time curves (for isothermal annealing), and plotting these values as a function of the appropriate temperature or time. They showed that the temperature or time at which the rate of change of hardness is a maximum coincides with the temperature or time at which 50% recrystallisation was observed metallographically, regardless of the amount of recovery-softening which may have occurred. Similarly, the temperature or time at which the rate of change of hardness decreases to zero was found to correspond to the completion of recrystallisation determined metallographically.

1.4.2. The nucleation of grains during primary recrystallisation.

1.4.2.1. General aspects.

It is clearly apparent from the considerable amount of investigations into the topic that no single theory of nucleation is applicable to all cases of primary recrystallisation. This is not unreasonable in view of the wide range of sub-structures formed during deformation. (See section 1.2.2.).

The experimental observations of nucleation have been summarised by Cahn (56, 60).

(a) Nuclei form preferentially in regions where the local degree of deformation is highest; such sites include grain boundaries, deformation bands, inclusions, twin intersections and free surfaces.

(b) The rate of nucleation increases sharply with increasing strain, above a minimum critical strain.
(c) There is extensive but not entirely conclusive evidence that the orientations of nuclei have a statistical correlation with the orientations of the deformed regions in which they form.

(d) It is very difficult to make generalisations about the variation of nucleation rate with time. The rate of nucleation may be constant or decrease with time. Occasionally, it increases with time. There may or may not be an induction period. The factors governing the time variation of the nucleation rate have not yet been clarified.

The theoretical models that have been advanced to account for these experimental observations will now be outlined. Recent experimental evidence on the process of nucleation has been reviewed by Doherty and Cahn (169).

1.4.2.2. The classical nucleation model.

Classical nucleation theory was first applied to recrystallisation by Becker (1), and, later, by Orowan (61). Their arguments have since been reviewed and criticised by Burke and Turnbull (4), Oriani (62) and Bailey (63).

The model is based on the idea that fluctuations in position of a group of atoms will occasionally, by chance, generate an embryo. In thermodynamic terms, the stability of the embryo depends on the balance between the increase in surface energy (due to the formation of a new surface) and the decrease in the volume free energy (due to the creation of a volume of lower internal energy material).

The change in free energy on forming an embryo is, therefore, given by:

\[ \Delta F_I = 4 \pi r^2 \psi - \frac{4}{3} \pi r^3 \Delta F \]

where

- \( \Delta F_I \) = total free energy change;
- \( r \) = embryo radius
- \( \psi \) = specific interfacial free energy change
- \( \Delta F \) = bulk free energy change.
As the two free energy terms have opposite effects on the total free energy change, there will be a critical radius above which the embryo will become stable and grow. This is found by differentiating equation (6) with respect to $\tau$ and equating the result to zero. The critical radius is, therefore, given by:

$$r_c = \frac{2\psi}{\Delta F} \quad \ldots(7)$$

and the change in total free energy required to form an embryo of this size is:

$$\Delta F_{tc} = \frac{16 \pi \psi^3}{3\Delta F^2} \quad \ldots(8)$$

In the case of primary recrystallisation, the volume free energy change is represented by the difference in strain energy between the cold-worked and fully recrystallised states. On this basis, the incubation period observed during isothermal annealing is the average time required for a series of thermally activated fluctuations to give rise to the creation of a strain region equal to, or greater than, the critical size for stability. The strain-free region can then be described as a viable nucleus, which can grow into the surrounding deformed matrix. The critical embryo radius, therefore, represents the minimum radius for a viable nucleus. This is given by:

$$r_c = \frac{2\phi}{E} \quad \ldots(9)$$

where $\phi$ = interfacial energy of the boundary between strained and recrystallised regions

$E$ = stored energy of cold-work.

Similarly, the free energy change accompanying the formation of viable recrystallisation nuclei is:

$$\Delta F_{tc} = \frac{16 \pi \phi^3}{3E^2} \quad \ldots(10)$$

It follows from Turnbull and Fisher's (64) treatment of a conventional phase transformation that the nucleation frequency, $N_e$, in a region of strain, $e$, is given by:

$$N_e = \frac{-\Delta F}{kT} \frac{16\pi\phi^3}{3kTE^2} \quad \ldots(11)$$

where $i$ = number of atoms of the mother phase per unit volume

$h$ = Planck's constant
\( T = \) absolute temperature
\( \Delta F = \) free energy of activation for grain-boundary self-diffusion
\( k = \) Boltzmann's constant

Burke and Turnbull (4) calculated the minimum size of a viable nucleus in copper on the basis of a model of homogeneous elastic shear, which would give rise to the formation of tilt-boundaries. They estimated the variation of the minimum radius of a viable nucleus with strain to be as shown in Figure 13. Their results showed that for this nucleation model to be realistic, very large local concentrations of strain energy had to be postulated, i.e. elastic strains of the order of 0.20 over regions a few Angstroms in diameter were required. Orowan (61) showed that the activation energy for this process is \( 10^8 \) eV. According to Cahn (60), even if the local stored energy of cold-work was greater by a factor of 10, the activation energy would still be \( 10^6 \) eV and the critical nucleus radius would become \( 500 \) Å, values which are still impractically large.

The theory also predicts that new grains should form with low misfit angles relative to the deformed matrix in order to have low interfacial energy values. However, it is often found that the orientation of new grains differs considerably from that of the cold-worked region in which they form.

The theory does, nevertheless, account for the existence of an incubation period and it also gives reasonable values of the nucleation frequency. However, the objections against it make it highly unlikely that nucleation occurs by homogeneously distributed thermally activated fluctuations within the deformed metal.

1.4.2.3. Preformed nucleus models.

It is clearly evident that, in some materials at least, nuclei must be preformed in the sense that the location of a nucleus is predetermined, not that it is ready to grow at once.

1.4.2.3.1. "Block" theories of nucleation.

The difficulties of applying classical theory to the nucleation of primary recrystallisation grains led Burgers (65) to postulate that the nucleus is a pre-existing "block" within the deformed metal.
In the "low-energy block" theory, the "block" is said to be a volume of material in which the strain is less than average. It is based on the concept that the interior of the "block" already possesses the stable structure of a recrystallised region and that it is ready to grow once the appropriate energy is provided by annealing. However, it is highly unlikely that regions of a cold-worked metal will completely avoid deformation as required by this theory, and there is hardly any experimental evidence to confirm the existence of strain-free regions in a deformed metal.

In the "high-energy block" theory, the strain in the "block" is said to be larger than average, and recrystallisation is initiated by a series of events which relieve the strain inside the "block". In other words, there is a gradual healing of a severely distorted region until it becomes perfect enough to acquire the thermodynamic ability to expand, and consume the initially less strained surrounding regions.

The mechanism of healing of a pre-formed nucleus has been the source of much speculation, and it was not until the theory of polygonisation was postulated that a clearer picture began to emerge.

1.4.2.3.2. Polygonisation and cell-growth theories. (See section 1.3.1.)

Beck (66) and Cahn (47) independently proposed that polygonisation of a region with a high dislocation density should result in a group of dislocation-free sub-grains, one of which would become a viable nucleus and grow into the surrounding matrix. Views on this model differ, and even electron microscopy has yielded no tangible evidence one way or the other.

A more realistic version of this model is based on the concept of a sub-grain growing in a recovered cell structure (6). If there is a steady shift in orientation across a region of the cell structure, the wall of the particular cell growing accumulates more and more dislocations. Eventually, it becomes a mobile high-angle boundary, which then begins to migrate rapidly and recrystallisation has begun. It is not clear, however, how the sub-grain boundary maintains its mobility before becoming a high-angle boundary.

The clearest experimental evidence for this kind of nucleation has been presented by Walter and Koch (67), who examined the recrystallisation of
heavily cold-worked iron-silicon crystals of initial cube orientation. A succession of well defined deformation bands were formed on rolling. Their crystallography was such that the transition zones between the bands were populated by a single type of edge dislocation. On annealing, sub-grains formed in these zones by polygonisation and they then grew. When one cell became large enough, its acquired high-angle boundary migrated rapidly, and recrystallisation began.

1.4.2.3.3. Sub-grain coalescence by rotation model.

Hu (49) examined identical crystals to those studied by Walter and Koch (67). After a cold-rolling reduction of 70%, his specimens were examined in a hot-stage electron microscope at 600°C. Small sub-grains were produced, and they grew in size on heating to higher temperatures before recrystallisation occurred. Hu, however, reached the conclusion that the sub-grains coalesce rather than develop by the growth of some at the expense of others. To account for this, he postulated that successive sub-grains rotate and become merged with their neighbours (68, 69). Hu explained the difference in orientation between the coalesced group and the original sub-grains from which it was formed as a gradual movement of dislocations out of the disappearing sub-boundary into the other boundaries around the sub-grains. This requires some dislocation climb along the disappearing boundary and a rotation of the sub-grain itself, with the movement of some of the atoms situated immediately around the relevant boundaries.

Li (70) thoroughly examined the possibility of sub-grain rotation during recrystallisation, and Figure 14 is a schematic representation of his model. He analysed the thermodynamic implications of this mechanism in terms of the misorientation angles and energies of the sub-grain boundaries. When he had shown that the mechanism was energetically feasible, Li went on to analyse its kinetic aspects. In doing so, he showed that the rate-controlling process can be either the co-operative diffusion of vacancies in the lattice or the co-operative movement of dislocations in the boundaries, depending on the misorientation angle of the boundary.
1.4.2.3.4. Geometric coalescence model.

This model has been applied to a large number of annealing phenomena in metals (71). Its basic idea is that if two neighbouring cells meet at a point, they may coalesce to form a single, larger cell, the diameter of which is equal to the sum of the diameters of the original cells.

For the nucleation of grains during primary recrystallisation, Nielson (71) postulates the coalescence of two neighbouring sub-grains which have similar, but not necessarily identical, orientations. When the external dihedral angles of the "new" enlarged sub-grain have approached equilibrium, the coalesced pair will have increased in volume by a considerable amount. The coalescence is said to occur by the movement of atoms from outside to inside the merging pair of sub-grains. According to Nielson, some pseudo-coalescences (which he defines as the merging of sub-grains of widely dissimilar orientations) will have to occur along with the regular geometric coalescence of sub-grains. The first pseudo-coalescences would not necessarily produce runaway grains, but they would produce large enough complex grains to allow them to survive and occasionally grow. Those that do grow would meet other pseudo-coalesced sub-grains of similarly related orientation. After a series of such meetings a run-away grain is established and this, says Nielson, must be the origin of a primary recrystallisation grain.

1.4.2.3.5. Comparison of pre-formed nucleus models.

The direct formation of nuclei by polygonisation is now thought to be a much less general possibility than when the model was first proposed. However, it, or something like it, may well play an important role in the final creation, during annealing, of the well defined sub-structure needed for other nucleation models to become operable; for example, the coalescence and bulge (see section 1.4.2.4.) models. Also, polygonisation remains an important direct possibility for the formation of nuclei in cases where a relatively small number of slip processes have been involved (72).

The choice between the sub-grain growth and sub-grain coalescence by rotation models rests upon the interpretation of some weak contrast between neighbouring fields in certain electron micrographs. Even a detailed discussion between Walter and Koch and Hu (73) has not produced a final and unambiguous
explanation. Nevertheless, Walter and Koch's interpretation does not invalidate Hu's general postulation of sub-grain coalescence by rotation as an important nucleation mechanism in primary recrystallisation. In fact, Walter and Koch (67) agree that sub-grain coalescence may be significant in many cases, whilst Hu (68) clearly acknowledges that localised boundary migration is a necessary cog in the process.

Recent work by Smith and Dillamore (74) suggests that sub-grain coalescence by rotation as considered by Li (70) is unlikely to occur in bulk metals as a contributory mechanism in sub-grain growth. They compared their experimentally determined times for one sub-grain coalescence with those predicted by Li's theory for the (111) [110] and (110) [110] orientations in high purity iron, and found the experimental sub-grain growth rate to be about four orders of magnitude faster than that predicted theoretically. Smith and Dillamore, however, emphasise that they have no results which can justify the complete rejection of sub-grain coalescence by rotation. In fact, Li's analysis has previously given order of magnitude agreement with the experimentally measured sub-grain growth rate for aluminium as determined by Beck et al. (75).

A comparison of the sub-grain coalescence by rotation mechanism and the geometric coalescence model reveals a basic difference. The former mechanism leads to the creation of increased misorientations around the sub-grain whereas the latter does not. Although a series of geometric coalescences may produce a strain-free region of super-critical size, it is not likely to produce surrounding high-angle boundaries where such boundaries did not exist originally. It is, therefore, difficult to see how geometric coalescence alone can account fully for the formation of a recrystallisation nucleus. However, it is probably involved in nucleation as part of rotation coalescence as it describes the surface tension phenomena involved in the boundary adjustment which removes the re-entrant angles in the boundaries surrounding the coalesced sub-grains (See Figure 14 d).

All the models imply the existence of an induction period and are by their very nature a form of oriented nucleation.

1.4.2.4. The martensitic nucleation model.

A fundamentally different process that has been proposed for nucleation
Fig. 13. Minimum radius for a viable nucleus as a function of strain for copper.

Fig. 14. Schematic representation of sub-grain coalescence by rotation.

Fig. 15. Schematic representation of strain-induced boundary migration.
is the possibility of a quasi-martensitic shear in small regions of the deformed lattice. Burgers and Verbraak (76) postulated this mechanism to cater for the specific case of the creation of a cube texture during the annealing of heavily deformed copper. However, there is no direct metallographic confirmation that localised shears of the type postulated do occur, and energy considerations indicate that the physical validity of the mechanism is extremely doubtful, even for the formation of the cube texture in copper.

This model must, therefore, be viewed with a great deal of reserve.

1.4.2.5. The bulge nucleation model.

The first detailed description of nucleation at grain boundaries was given by Beck and Sperry (77). They showed that in high-purity aluminium, after cold-rolling deformations of up to 40%, the formation of "new" nuclei on annealing is very rare, and that the volume elements which are substantially free of sub-structure form by the "strain-induced migration" of already existing boundaries.

Separate kinetic experiments (78) indicated that there was no incubation period during this form of recrystallisation, and that the boundary migration rate was highest initially and then decreased with increasing annealing time. This is not surprising since there is no nucleation at all in this process; an existing grain merely advances into its neighbouring grain and, in the process, becomes strain-free.

Figure 15 represents 'Beck's model' (5) for this form of boundary migration. It is assumed that the boundary between the two grains A and B is capable of high mobility, and that there is a significant strain difference between the two grains. The high dislocation concentration in grain B is shown schematically as a fine sub-grain structure while grain A, which is growing, is shown as having a much coarser structure. Under these circumstances, the migration of the boundary is said to be initiated by that part of its length which forms a boundary to one of the large sub-grains (5) in grain A. The direction of migration is away from this grain into grain B. This leads to a reduction in internal energy which is equivalent to the difference between the stored energy released in the consumed region and the energy required to extend the length of the migrating boundary. The driving force for the process is provided by
the difference in stored energy between the two grains, A and B. Aust and Dunn (79) have confirmed this model by revealing sub-boundaries in silicon-iron on both sides of a grain boundary which was in the process of strain-induced boundary migration.

Vandermeer and Gordon (80) also studied the isothermal recrystallisation of pure aluminium at deformations up to 40%, and observed that all new grains were nucleated in clusters at sites along the grain boundaries of the deformed structure. Only a small proportion of the total grain boundary area produced nuclei. This appears to be inconsistent with Beck and Sperry's observations. However, lattice distortions very near to a deformed grain boundary can be very substantial (often implying more deformation than in the grain interiors (32)), and it is quite conceivable that the sub-structure adjacent to a grain boundary varies considerably in orientation along the length of the boundary (60). Vandermeer and Gordon also found that new grains began to grow at the beginning of the annealing process, with no incubation period. In effect, this rules out any other type of nucleation process. It is, therefore, likely that nucleation in this series of experiments was by strain-induced boundary migration.

Bailey and Hirsch (17, 63, 81) used electron microscopy techniques to examine the different stages of the deformation and annealing behaviour of copper, nickel, silver and gold. Recrystallisation occurred by the formation and growth of bulges of local regions of the grain boundaries. The advancing bulges were about 1 micron across for copper, compared with about 20 microns for Beck and Sperry's (77) aluminium. This is probably because the aluminium had a much larger initial grain size than the copper. Bailey and Hirsch noted that the regions inside the bulges, through which the boundaries had migrated, were virtually free of dislocations. This led to the stipulation that segments of the grain boundaries should have few, if any, dislocations terminating on the low strain side for them to be able to migrate.

Bailey (63) developed a detailed analysis of this form of nucleation. The process was envisaged to occur by the bulging of boundary segments, of length 2L, to form spherical caps, of radius R, which then continue to migrate. Figure 16 illustrates schematically successive stages of migration. The basic condition for a bulge to grow is given by:

\[ L > \frac{2S}{AE} \]  

...(12)
where \( S \) = the surface energy of the migrating boundary

\[ \Delta E = \text{the difference in stored energy, per unit volume, across the migrating boundary}. \]

When known quantities are substituted into this expression, the predicted critical length of a visible bulge in silver deformed 25% is about 0.5 microns. This compares satisfactorily with the lengths Bailey actually observed (1 micron) in cold-worked and annealed silver.

Bailey and Hirsch (81) further showed that this mechanism of nucleation is compatible with the normal kinetics of the recrystallisation process, which usually follows the Avrami equation (82):

\[ 1 - X = e^{-Bt^K} \]

where \( X = \text{volume fraction of material recrystallised} \)
\( t = \text{annealing time} \)
\( K = \text{index related to the location of nucleation sites and the growth habit of new grains.} \)

In particular, the growth rate was shown to pass through a minimum when \( 2\alpha = 180^\circ \). (See Figure 16). The rate of growth of the bulge will be slow initially, with a marked acceleration once the bulge has become larger than a hemisphere. Qualitatively, this initial period of slow growth can be taken as an induction period. Quantitatively, however, Bailey's analysis showed that, for metals with a well developed sub-structure, the time involved will be short compared to the time scale on which recrystallisation kinetics are usually measured.

There seems to be little doubt of the importance of the bulge nucleation mechanism, and it is common in moderately deformed, fine-grained metals. It is consistent with the observation that nuclei under such conditions form exclusively along grain boundaries, and also with the zero induction period noted for such materials. The observations of recrystallisation from deformation twins are also consistent with the operation of the bulge nucleation mechanism. A non-coherent twin boundary, for this purpose, is considered equivalent to a normal high-angle boundary.

1.4.3. The growth stage of primary recrystallisation

The growth stage of primary recrystallisation consists essentially of the
migration of high-angle boundaries, surrounding the expanding new grains, through the deformed structure.

The first theories of grain boundary migration were developed by Mott (83) and Turnbull (84) on the basis of the absolute reaction rate theory. Turnbull assumed that atoms are transferred singly across the migrating boundary. This leads to a relationship of the form:

\[ G = G_0 e^{-Q/RT} \]  

where  
- \( G \) = the rate of migration  
- \( Q \) = activation energy  
- \( R \) = gas constant  
- \( T \) = the absolute temperature.

\( G_0 \) is a function of

(a) the distance of local boundary movement when an atom is transferred from one grain to the other,

(b) the lattice parameter,

(c) the driving force, and

(d) the temperature.

The majority of experimental results are consistent with this relationship.

Turnbull (84) suggested that the activation energy barriers involved in his model are similar to those for grain boundary self-diffusion, and that the rate determining step for boundary migration is related to the diffusion coefficient for atom transport along the boundary. By comparing the relevant free energies, he reached the conclusion that the atomic mobility in grain boundary migration should be several orders of magnitude larger than that in lattice self-diffusion, and that the entropy change in migration should be close to zero. However, measurements of the temperature dependence of boundary migration rates have shown that the entropy change is often large, and that the activation energy is sometimes of the same order of magnitude as that for lattice self-diffusion. Turnbull attributes these anomalies to the retardation of boundary migration by the effect of impurities, which may become less as the temperature is increased. This theory is referred to as the "single process theory", and a similar model has been developed by Beck, Sperry and Hu (85).
Mott (83) attempted to account for the high values measured for entropy and activation energy on the basis of his "group process theory". He assumed that atoms are activated in groups during transfer across a grain boundary and that the basic process involves the melting of a group of atoms belonging to one crystal followed by their re-solidification on the other crystal. This leads to a relationship, similar to equation (14), in which $G_0$ is related to the number of atoms in the transferring group. There is, however, no reason to suppose that atom transfer during boundary migration occurs in groups rather than singly (86), and it is generally accepted that the basic process can be explained by variations of Turnbull's "single process theory" (86, 87).

Li (88) has proposed different mechanisms to account for the migration of low- and high-angle grain boundaries. He suggested that the mobility of low angle boundaries depends on the mobility of the dislocations which comprise the boundary, and that such movement becomes more difficult as the misorientation increases. The mobility of a large-angle boundary is considered to be dependent on the movement of individual atoms in the grain boundary, and it increases as the degree of "porosity" in the boundary increases with increasing misorientation. This raises the importance of vacancies to grain boundary migration. A grain boundary, as well as being a source of vacancies, is also a vacancy sink, and the migration of the boundary is expected to be dependent on vacancies. There is indirect evidence from boundary migration measurements that vacancy absorption can alter a boundary to such an extent that its migration rate increases dramatically (6).

Gleiter (89, 90) formulated a theory of boundary migration, on the basis of his observations that the surfaces of adjacent grains in aluminium consist of a pattern of small steps. Migration is said to occur by the emission of atoms from the steps on the surface of the shrinking grain into the boundary, and the absorption of a similar number of atoms from the boundary on to the steps of the surface of the growing grain. This leads to the movement of the steps on the surface of both grains such that one grain shrinks and the other grows. However, the widespread application of Gleiter's model is open to doubt, as Levy (91) has pointed out that the interpretation of electron contrast effects at grain boundaries, (upon which this model depends) should be undertaken
with great caution, and that boundary migrations have been observed in aluminium for grain boundaries which did not show the contrast effects discussed by Gleiter. It is, therefore, probable that Gleiter's model is valid in certain special cases, but it is not necessarily a universal description of grain-boundary migration in general.

Aust and Rutter (92) compared their data for zone-refined lead with the theories of Turnbull and Mott. They clearly showed that, with impurities present, neither theory correctly predicted the boundary migration rate. But, when impurity effects were absent, Turnbull's "single process theory" gave order-of-magnitude agreement with the experimental data, whereas Mott's "group process theory" did not. Similar findings have been quoted for aluminium (93). It, therefore, appears that the basic process in grain boundary migration involves the transfer of single atoms across the boundary.

The effect of impurities on grain boundary migration will be discussed in Sections 1.4.6.2.3. and 1.4.7.4.

1.4.4. The kinetics of primary recrystallisation.

Ever since the early work of Mehl et al. (94, 95), recrystallisation kinetics have been described in terms of the rate of nucleation and the linear rate of grain boundary migration. Such studies indicate that recrystallisation progresses in a sigmoidal manner with respect to time. There is an initial incubation period, followed by a rate of change which is initially slow, then accelerates, and finally becomes slow again as the process is completed. A typical curve is shown in Figure 17. The incubation period is generally associated with the initial formation of nuclei, although, in some cases, it is absent. (See section 1.4.2.5.). It has been reported that increasing the time of isothermal annealing during recrystallisation increases the rate of nucleation and decreases the rate of grain boundary migration (96); increasing the temperature increases the boundary mobility (95); and increasing the amount of deformation increases both the rates of nucleation and growth (94, 95).

Avrami (82) proposed the theory that a fixed number of pre-formed nucleation sites exist in the deformed metal and that the nucleation rate remains constant throughout recrystallisation. This leads to a relationship of the form
Fig. 16. Schematic representation of grain-boundary bulging.

Fig. 17. Recrystallisation kinetics for aluminium.

Fig. 18. Nucleation and growth rates as functions of prior deformation for aluminium annealed at 350°C.
\[ X = 1 - e^{-Bt^K} \]  
\( X \) = fraction recrystallised  
\( B \) = constant of the form \( B = B_0 e^{-Q/RT} \)  
\( t \) = annealing time  
\( K \) = constant depending on specimen dimensions.

For bulk specimens, \( K \) lies between 3 and 4; for thin sheets, between 2 and 3; and for wires, between 1 and 2. An equation of this form is agreed upon by most workers.

Johnson and Mehl (97), however, pointed out that the nucleation rate is not constant, and that it is more accurate to make experimental measurements than to assume any particular mathematical form. On this basis, Mehl et al. (94, 95) found that the nucleation behaviour of aluminium, previously deformed 5.1% in tension, to be of the form

\[ N = a e^{bt} \]  
\( N \) = nucleation rate  
\( t \) = annealing time  
\( a \) and \( b \) = constants.

They also found that, in this case, the growth rate is not a function of time, although it is time-dependent. By comparing their experimental results with the theoretical predictions for recrystallisation in bulk specimens, they obtained fairly good agreement. Any minor discrepancies were explained in terms of the possible orientation dependence of the growth rate.

1.4.5. General factors which influence recrystallisation.

The process of primary recrystallisation is dependent on several variables:

(a) metal purity (see sections 1.4.6. and 1.4.7.)
(b) the conditions of deformation
(c) the time and temperature of annealing (see sections 1.4.6. and 1.4.7.)
(d) the original grain-size
1.4.5.1. The amount of prior-deformation.

Burke and Turnbull's laws of recrystallisation (4) (see section 1.4.1.1.) indicate that primary recrystallisation depends on the extent of deformation prior to annealing. The reasons for this are that the driving force for recrystallisation is provided by the high internal energy of the deformed metal, and that the detailed phenomena in the nucleation and growth of new, recrystallised grains are closely dependent on the distribution of strain within the metal. However, thermal energy has to be supplied before these processes are activated. This leads to the concept of a recrystallisation limit, which has been defined as the lowest temperature which produces complete recrystallisation for a specific metal and condition (98). This property shows the effect of strain on recrystallisation in two ways. First, there is a minimum strain below which recrystallisation does not occur. Secondly, increasing the strain above this value lowers the temperature of the recrystallisation limit. The minimum strain for recrystallisation arises from the need to provide a structure in which nucleation can occur and which has sufficient strain energy to activate the migration of the high-angle boundaries surrounding the nuclei.

The effect of strain on the recrystallisation limit is usually interpreted in terms of changes in the rates of nucleation and growth. A good example of this is provided by the work of Mehl et al. (94, 95) on aluminium (see section 1.4.4.). Figure 18 shows that the nucleation rate is low for strains up to about 7%, but then rises steeply as the strain is increased. The growth rate, however, varies with strain in a sigmoidal manner. In particular, it increases rapidly with strain up to about 10%, and then becomes constant at strains greater than about 15%. Therefore, both the nucleation and growth rates are most sensitive to changes in strain at low strains (up to about 15%), although the growth rate eventually becomes an insensitive function of strain while the nucleation rate is increasing rapidly (4).

When metals recrystallise after low strains, large grain-sizes are produced. The strain which produces the largest grain-size is usually slightly larger than the minimum strain for recrystallisation. It is referred to as the critical strain, and the resultant grain-size is the critical grain-size. It has generally
been found that the critical strain decreases as the annealing temperature or
time increases, and it increases as the impurity content of the metal increases
(99).

### 1.4.5.2. The original grain-size.

It has been shown (section 1.2.4.4.) that a variation in the initial grain-size
has a significant effect on the dislocation density after deformation. Experi­
mental evidence to substantiate a dependence of recrystallisation kinetics on
original grain-size comes from two sources - stored energy measurements
and direct recrystallisation studies.

Evidence that the stored energy of cold-work is a function of grain-size
has been discussed in section 1.3.4. In particular, Clarebrough et al. (44)
have shown that the stored energy is greater in fine-grained copper (99.98% pure)
than in the coarse-grained metal, but only up to 38% deformation. Above this
deformation, the total stored energy is the same for both grain-sizes. The
energy is also released more rapidly in the fine-grained metal. However,
they found that the recrystallisation temperature is always lower in the
fine-grained metal even when the stored energy is equal for both grain-sizes.
They suggested that the segregation of impurities to the grain-boundaries in
the coarser-grained metal could account for this strange recrystallisation
behaviour at large strains. Loretto and White (57) worked in a similar manner
on a copper of higher purity (99.999% pure). One of the grain-sizes they
used was the same as Clarebrough's coarse grain-size. A comparison of the
two sets of data supports the suggestion that segregation of impurities is an
important factor in controlling the recrystallisation behaviour of the less pure
copper used by Clarebrough et al.

Cook and Richards (100) made a detailed study of the recrystallisation
kinetics for copper having two different grain-sizes. They observed the
highest recrystallisation rate to be produced by the finest grain-size.
Doherty and Martin (101) have provided evidence that, in two-phase alloys,
isothermal recrystallisation rates are increased by an increase in grain-
boundary area (See Figure 19.).

The role of grain-boundaries in the recrystallisation of an aluminium -
5.75% zinc - 1.95% magnesium alloy has been described in detail by Ryum (102). He assumed that, in this alloy, it is possible to obtain variations in the dislocation structure for a given strain, without altering the overall driving force for recrystallisation. He altered the dislocation structure by varying the degree of precipitation before straining. On annealing, he found that the formation of a well-defined sub-structure and the subsequent occurrence of primary recrystallisation takes place more rapidly in specimens with a heterogeneous dislocation distribution than in others. The acceleration was particularly associated with an increase in nucleation rate as a result of localised nucleation in regions near to the grain-boundaries where the sub-structure is particularly clearly defined.

It is, therefore, clear that the grain-size of a metal influences its recrystallisation behaviour in two ways. Firstly, it affects the overall dislocation density of the deformed metal, and, secondly, it leads to variations in the amount of grain-boundary regions at which nucleation can occur. All the nucleation mechanisms (described in sections 1.4.2.3. and 1.4.2.5.) can account for the initiation of nucleation at, or near to, grain boundaries. In general, the finer the grain-size of a metal before cold-work, the greater is the rate of nucleation and the smaller the recrystallised grain-size for a given amount of deformation.

1.4.6. Primary recrystallisation in solid-solution alloys.

1.4.6.1. Experimental observations.

Since Chandron (103) reported that the recrystallisation temperatures of "super-purity" and 99.99% pure aluminium differed by about 100°C, much experimental work on the effect of alloying elements on recrystallisation has been carried out. However, the comparison and interpretation of data from different sources is made difficult by the influence of the following factors which affect recrystallisation behaviour:

(a) the difficulty of standardising purity levels
(b) the use of different deformations prior to recrystallisation
   (See section 1.4.5.1)
(c) the use of different experimental techniques to follow recrystallisation behaviour (See section 1.4.1.2.)
the use of different initial grain sizes (See section 1.4.5.2.)
the use of different definitions of the recrystallisation temperature.
Consequently, the formulation of a comprehensive theory for impurity-controlled recrystallisation is very difficult.

The bulk of experimental work has been carried out on solid-solutions based on aluminium which is extremely sensitive to the effects of impurities. One of the earliest systematic investigations of the effect of small additions was made by Chosset (104). He showed that the course of recrystallisation is strongly influenced by the first traces of solute (less than 0.01 %), especially with heavy prior deformations. Larger amounts of impurity (about 0.1%) were found to have a much smaller effect.

In order to determine which impurities were responsible for the increase in recrystallisation temperature, Blade et al. (105) produced alloys with controlled amounts of several solutes by levitation melting. This technique avoided any contamination by extraneous material from melting crucibles and oxidising atmospheres. They found that all the solutes raised the recrystallisation temperature of super-pure aluminium; silicon, copper and magnesium by less than 100°C, and manganese, iron and chromium by about 200°C.

1.4.6.2. Theoretical interpretations.

1.4.6.2.1. General aspects.

Experimental evidence has been presented in section 1.4.6.1. to show the effect of solute atoms on the recrystallisation behaviour of a metal. In general, solutes retard recrystallisation to an extent which depends on the nature and quantity of the solute. Evidence is available which suggests that the change in recrystallisation as a function of composition cannot be represented by any single linear relationship for the entire solid-solution range of a given alloy system. Above certain solute concentrations, a different linear relationship may often be applicable, usually with a smaller degree of retardation than that which occurs at low solute concentrations.

The interpretation of the experimental data has been confined almost entirely to the growth stage of recrystallisation, and hardly at all to the nucleation stage. The theories that have developed are based on the
direct influence of solute atoms on grain boundary mobility. These theories will be discussed in section 1.4.6.2.3. However, the possible influence of solute content on the nucleation stage will be discussed first.

### 1.4.6.2.2. Solute dependent nucleation.

Masing et al. (106) determined recrystallisation rates for aluminium-manganese alloys, and observed that both nucleation and growth rates decreased to the same extent for manganese concentrations up to 0.01\%. Lücke and Detert (107) concluded from this that the same elementary process affected both the nucleation and growth stages. They, therefore, only considered solute limited grain boundary migration when forming their theory (Section 1.4.6.2.3.). However, increasing the manganese content up to 0.1\% decreased the nucleation rate less than the growth rate.

Leslie et al. (108) considered that, in iron alloys, solutes are able to stabilise dislocation arrays or low-angle boundaries so that their growth or coalescence to form recrystallisation nuclei is delayed. In this way, the solutes delay the nucleation stage of recrystallisation. They also pointed out that solutes alter the type of dislocation structure formed after cold-working and that solutes have been observed to enhance or prevent sub-grain formation after cold-working. Evidence for the occurrence of the latter effect is provided by the reduction in stacking-fault energy caused by solute additions. This influences the perfection and size of sub-cells.

In spite of the experimental evidence that the nucleation stage of recrystallisation is more difficult for impure materials compared with pure metals, a general theory for solute dependent recrystallisation (taking into account the influence of solutes on nucleation) has not been formulated.

### 1.4.6.2.3. Solute dependent growth.

The large discrepancies between the predictions of the single process theory (see section 1.4.3.) and experimental data for cases other than zone-refined samples shows that impurities have an important role in the mechanism of boundary migration which is not explicitly accounted for in Turnbull's theory (84). Consequently, several explanations for this aspect of recrystallisation have been proposed, the difference between them being mainly
Fig. 19. Apparent nucleation rate as a function of particle spacing for both polycrystalline $\Delta$ and monocrystalline $\bigcirc$ aluminium-copper alloys.

Fig. 20. Schematic variation of migration rate with temperature for constant driving force and composition.

Fig. 21. Schematic variation of migration rate with composition for constant driving force and temperature.
in the detailed form of the interaction between the solute atoms and the
migrating boundary.

1.4.6.2.3.1. The Lücke and Detert theory of impurity-dependent
grain boundary migration.

Lücke and Detert (107) were the first to attempt a quantitative theory for
impurity-controlled boundary migration. They assumed that impurity atoms
segregate to grain boundaries; that is, the boundary is an energy sink for
impurity atoms. When migration of such a boundary takes place, the impurities
are dragged along as an atmosphere near to it. The speed of migration is then
dependent on the rate at which impurity atoms diffuse along behind the boundary.
According to this theory, if the driving force is large enough to overcome
the dragging effect of the impurities, then, at low impurity concentrations or
high temperatures, the boundary breaks away from the impurity atmospheres
by the mechanism of solvent atom diffusion across it; that is, the boundary is
able to move independently of the solute atoms at low impurity concentrations or
at high temperatures. The breakaway process should be very abrupt and should
occur at certain critical values of composition, driving force and temperature.
It was, however, appreciated that in reality there would be a gradual transition
region in which the boundaries only partially break away. Figure 20 is a
schematic representation of the variation in boundary migration rate with
temperature for a constant driving force and composition. Figure 21 shows
the variation in boundary migration rate with composition for a constant driving
force and temperature.

The Lücke and Detert theory has accounted for the experimental observations
for many metal solvent-solute systems e.g. alloys of copper in zone-refined
aluminium (93). However, one of the main failures of the theory is its inability
to explain Aust and Rutter's results on the effect of tin (92, 109) and silver and
gold (110) in zone-refined lead. Aust and Rutter found that boundaries with a
Kronberg-Wilson or other "special" orientation relationship to the crystal being
consumed are less sensitive to impurity atoms than boundaries with "random"
orientations (Figure 22). (Kronberg and Wilson (111) proposed that, for
certain orientations, both grains have a partial lattice in common.) They also
found that silver and gold are much more effective than tin in retarding boundary
migration (Figure 23). This is in direct opposition to the predictions of the
Lücke and Detert theory which says that, as silver and gold diffuse faster than
tin in lead, they should exert less of a drag and allow the boundary to move faster. Holmes and Winegard (112) also raised objections when they used the theory to calculate solute diffusion coefficients from their growth rate data and found that the calculated rates were about two orders of magnitude too large.

1.4.6.2.3.2. Modifications to the Lücke and Detert theory.

The main assumptions, approximations and limitations of the Lücke and Detert theory are (86):

(a) It predicts that breakaway from an impurity atmosphere is an abrupt process.
(b) It assumes that the boundary velocity is equal to the velocity of the impurity atoms.
(c) It assumes that the grain boundary-impurity concentration is given by the stationary equilibrium value and does not alter when the boundary moves.
(d) It only considers segregation in which impurity atoms are adsorbed at boundaries.
(e) It assumes that diffusion of the impurity atoms controls the solute-dependent migration behaviour.
(f) It does not acknowledge that the boundary-impurity interaction energy and the diffusion coefficient of the impurity vary as a function of the distance across the boundary.

Modifications to this theory are required to obtain a more satisfactory agreement with experimental data.

Gordon and Vandermeer (93) formulated a modification of the theory (for those cases where migration is not independent of solutes) to take account of local changes in atomic vibration frequencies when the solute atoms move into a boundary. They found a satisfactory agreement with the results of other workers (112, 113), but the same success was not achieved for the results of Aust and Rutter (92, 109, 110). They, therefore, considered the values of boundary migration rates determined by those workers to be inaccurate as orientation factors may have influenced their results.

A more rigorous re-interpretation of Lücke and Detert's theory was made by Lücke and Stiße (114). They studied in detail the diffusion of impurity atoms
in the "potential-field" of the grain boundary. The atmosphere of atoms was considered to evaporate as the velocity of the boundary increased. This modified theory accounted for experimental results more accurately than the original version.

Cahn (115) attempted to modify the Lücke and Detert theory by studying in greater detail the distribution of solute atoms in the region of the grain-boundary during steady-state migration. The application of this model to experimental observations involves the use of complex differential equations for which knowledge of the main functions is sparse (87). This theory is too restrictive in the sense that it does not allow a decision to be made from first principles as to whether a measured velocity or a given driving force is high or low (86).

1.4.6.2.3.3. Other theories of solute-dependent growth.

Machlin (116) considered that a moving grain boundary should become cusped at a point where it meets an impurity atom. He supposed that the rate-controlling step in the migration process is the diffusion of the impurity atoms along the cusped part of the boundary. He found the Aust and Rutter data (92, 109) on random single-boundary migration to be in complete agreement with his ideas. However, Lücke and Stäßwe (114) severely criticised this model on the basis of the theoretical assumptions used in its derivations.

Li (117) viewed the impurity effect on the basis that solute atoms segregate to the boundary to reduce its porosity. This theory leads to a saturation effect in the migration rate at high concentrations of solute atoms. However, to make a significant quantitative verification of this model, more information regarding the porosity of the boundary, with or without impurity atoms, is required.

In all the theories of solute dependent growth, boundary migration is said to be controlled by adsorbed solute atoms. However, a greater knowledge of boundary structure and properties is required for further development of the theories. This will enable values of solute/boundary interaction forces and atom mobility in, and adjacent to, grain boundaries to be obtained. The influence of solute concentration on boundary velocity needs to be determined for a wider range of solvent-solute systems. The general application of the existing theories may then be tested.
Fig. 22. Grain-boundary migration rate at 300°C as a function of weight percent tin for "random" and "special" boundaries in zone refined lead.

Fig. 23. Apparent activation energies of boundary migration as a function of weight percent tin for "random" and "special" boundaries in zone refined lead.

Fig. 24. The effect of decreasing solubility (as the temperature falls) of impurities on the annealing behaviour of Al
1.4.7. The primary recrystallisation of two-phase alloys.

1.4.7.1. General aspects.

Investigations of the annealing characteristics of two-phase alloys have shown that second-phase particles can either accelerate or retard recrystallisation compared with the behaviour of the particle-free matrix. The controlling factors appear to be the size and spacing of the dispersed particles. However, these parameters do not have an absolute value since particles are rarely uniform in size, shape, or distribution. Also, the inter-particle spacing has been calculated on the basis of many definitions and formulae, each producing a different value in a given alloy structure.

In many investigations, values of one or other of the controlling parameters are omitted, and the reported data does not allow their calculation. This, therefore, makes it difficult to compare recrystallisation behaviour in the various alloy systems.

The two-types of recrystallisation behaviour are reviewed separately below, and the evaluation of inter-particle spacing is discussed elsewhere. (Section 4.1.1.).

1.4.7.2. Accelerated recrystallisation.

Martin (118) has shown that the presence of dispersed silica particles in single crystals of copper accelerates recrystallisation. He found that increasing the volume fraction of silica lowers the recrystallisation temperature. He quoted inter-particle spacings in the range 8 to 24 μm. However, their meaning is not clear due to the large differences in diameter of the particles in his high silicon content alloy and those in the low content alloy.

Day (119) working on an aluminium - 1.35% manganese alloy with additions of silicon and iron, found that reduction of free manganese in solid solution and also coalescence of the second phase cause recrystallisation to occur at lower temperatures, and yield a finer final grain size. She considered this effect to be the result of the greater internal stresses, forming around the larger particles during deformation, aiding the formation of recrystallisation nuclei. She did not, however, interpret the effect in terms of changes in the inter-particle spacing.
Phillips and Phillips (120) observed that the presence of tellurium accelerates the recrystallisation of copper. The impurity was present as a finely dispersed phase. They found the acceleration to be greater for an alloy containing 0.00025 wt.% Te than for one containing three times as much.

Indirect evidence for the acceleration of recrystallisation due to the presence of precipitates is provided by the work of Richards and Pugh (121). They studied the influence of variation in intermediate annealing temperature on the recrystallisation behaviour of a commercial aluminium (99.4% Al + 0.29% Fe + 0.14% Si) during a final isothermal anneal at 250°C. Some of their results are shown in Figure 24, which indicates that the rate of recrystallisation during the final anneal increases steadily as the temperature of intermediate annealing is reduced from 500°C to 400°C. This is consistent with a steady decrease in solubility, as the temperature falls, and could be taken to imply particle-induced acceleration of recrystallisation. However, an alternative explanation for these results is that super-saturation of the solid-solution of some specimens retards recrystallisation by solute drag effects.

Other indirect evidence for enhanced recrystallisation is provided by Williams and Eborall (127) who investigated the effects of strain, annealing temperature and original grain-size on the critical strain and final recrystallised grain-size of several aluminium alloys.

Leslie et al. (108) examined a series of dilute iron-oxygen alloys containing varying degrees of dispersion of the second phase. They showed that isolated oxide inclusions, a micron or more in diameter, in an alloy deformed by 60%, are each associated with several new grains on annealing, and cause an acceleration of the entire recrystallisation process. Below this diameter, the particles tend to retard recrystallisation. Blade (123) similarly observed that a fine dispersion of Al$_3$Fe particles of about 1 μm diameter in aluminium alloys causes nucleation to be accelerated by a factor of ~10 and growth to be retarded by 2, so that recrystallisation as a whole is accelerated.

A good example of nucleation occurring at large inclusions has been provided by the work of English and Backofen (99), who studied the recrystallisation of iron-silicon alloys during hot-working. They found that new grains are formed at the inclusion/matrix interface before recrystallisation of the surrounding
material occurs. They also reported that the grain size after recrystallisation is smaller for the alloy containing the larger number of inclusions. This suggests that more nucleation sites become available as the number of particles increases.

Antonione et al. (125, 129) studied the influence of small amounts of carbon and nitrogen on the recrystallisation of high purity iron. Their specimens were cold-rolled 80% and then annealed both isothermally and isochronally. Their important results are summarised in Figures 25 and 26. It can be seen that additions of carbon and nitrogen in quantities above the limit of solubility in \(\alpha\)-iron at the recrystallisation temperature cause a noticeable increase in the nucleation rate. This is due to the presence of precipitated nitrides and carbides. Further work by the same research group (126) has shown that the effect of coarse oxide inclusions (up to 10 \(\mu\)m) in pure iron is also to increase nucleation rate. Consequently, recrystallisation is accelerated.

Doherty and Martin (122) studied the recrystallisation of two-phase aluminium-copper alloys. Although their work is mainly concerned with retarded recrystallisation (see section 1.4.7.3.), their data clearly shows that alloys with the largest inter-particle spacing (4 \(\mu\)m) recrystallise faster than the matrix solid-solution alloy. Humphreys and Martin (128) have also shown that the same dispersed phase can cause either an acceleration or retardation of recrystallisation. They found that, at 700\(^\circ\)C, the recrystallisation of cold-rolled single crystals of internally oxidised copper-silicon alloys is accelerated at inter-particle spacings greater than 1 \(\mu\)m, in comparison with that of single-phase crystals.

Mould and Cotterill (124) have made a comprehensive study of the annealing behaviour of two-phase aluminium-iron alloys. Their work has the merit of separating the effects of the dispersed phase and the matrix grain size on nucleation. All their alloys were first stabilised at 450\(^\circ\)C before a final reduction of thickness of 60\% by cold rolling. They used isochronal (for 1 hour) and isothermal (at 300\(^\circ\)C) annealing, to induce recrystallisation. The progress of recrystallisation was followed by hardness measurements and metallography. Some of their results are shown in Figures 27 and 28.
Fig. 25. Number of recrystallisation nuclei as a function of the fraction recrystallised for pure iron with different amounts of carbon and nitrogen.

Fig. 26. Rates of nucleation as functions of annealing time for pure iron with additions of nitrogen and carbon above their solubility limits.

Fig. 27. The progress of recrystallisation as a function of annealing time for various aluminium-iron alloys.
Examination of these results revealed that the two-phase alloys did not have a constant grain-size before recrystallisation. They, therefore, carried out supplementary tests on selected alloys to determine the effect of different matrix grain-sizes on the recrystallisation temperatures (Ti, T\textsubscript{1/2} and Tc). The grain-size dependence of these temperatures was found to be more pronounced for the alloys containing the least number of particles. Figure 29 illustrates the distinction in grain-size sensitivity between dilute and concentrated dispersions. Mould and Cotterill consequently corrected their results to a constant pre-recrystallisation grain-size of 0.14 mm, as shown in Figure 26. They concluded that recrystallisation is accelerated as the inter-particle spacing of the Al\textsubscript{3}Fe inclusions decreases from 15 \textmu m to 4 \textmu m, and/or as the original matrix grain-size decreases. They interpreted their results in terms of an increase in nucleation rate at particle/matrix interfaces and/or at the original grain boundaries with no significant change in the growth rate. A hypothesis was also proposed for the retardation of nucleation, observed by other workers, in more closely spaced dispersions (see section 1.4.7.3.).

In general, acceleration of the nucleation stage of recrystallisation has been qualitatively accounted for on the basis that the prior deformation causes increased local lattice curvature adjacent to the particles. The interfaces of the particles with the surrounding matrix then act as sites for the formation of recrystallisation nuclei. In this way, an increase in the number of particles enhances the nucleation rate. Recent work by Rollason and Martin (130) has shown that this effect is dependent upon the size and shape of the dispersed particles. They suggest that the particle size must be greater than 0.3 microns for the formation of nucleus embryos, and that embryos formed at coarse particles will only actually form nuclei if the inter-particle spacing is large enough (e.g. > 1 micron) (see section 1.4.7.3.).

1.4.7.3. Retarded recrystallisation.

All the reported cases of particle-retarded recrystallisation have occurred for alloys in which the inter-particle spacing has been of the order of a micron or less. The sizes of the particles, when quoted, have been much finer than a micron.
Fig. 28. Recrystallisation temperatures as functions of iron content for aluminium-iron alloys rolled 60% and isochronally annealed; corrected to a constant initial grain-size of 0.14mm.

Fig. 29. Number of recrystallisation nuclei as a function of the progress of recrystallisation for various aluminium-iron alloys.

Fig. 30. Hardness as a function of annealing temperature for copper-alumina and copper-silica alloys.
Extensive work has been carried out on the annealing characteristics of deformed metals containing a dispersed oxide. In general, the resistance to recrystallisation is greatly enhanced by the introduction of such dispersions.

Gatti and Fullman (131) investigated the recrystallisation kinetics of an internally oxidised silver-aluminium alloy. The diameter of the alumina particles was in the range 0.005 to 0.01 μm. They found that recrystallisation is retarded by the finely dispersed particles so that the increase in strength due to cold-work is retained on annealing at temperatures up to about 700°C. To account for inhibited recrystallisation, they proposed a mechanism based on the model of particle-induced restraint of mobile boundaries (see section 1.4.7.4.). They postulated that the growth of recrystallisation nuclei stops when they first encounter particles.

Grant and his co-workers (132-137) have reported on the recrystallisation behaviour of several internally oxidised alloys, mainly copper-alumina and copper-silica alloys. They have presented isochronal annealing data for these alloys, although none of their materials were previously cold-worked, the strength being due to the residual strain from extrusion and the presence of the particles. Typical results are shown in Figure 30. It can be seen that increasing the volume per cent of oxide (particle diameters in the range 0.01 to 0.03 microns) retards recrystallisation.

In particular, Chin and Grant (137) have correlated inter-particle spacing with recrystallisation temperature for copper-alumina alloys. They have shown that by decreasing the spacing from 0.5 to 0.06 μm, the recrystallisation temperature increases from 700°C to over 1000°C. Komatsu and Grant (136) reported an effect of particle size and prior deformation on the recrystallisation behaviour of a copper - 12 volume per cent silica alloy. They found that an alloy having an intermediate anneal at 800°C followed by 5% deformation recrystallises more easily than the as-extruded material. They interpreted this in terms of particle coarsening (increasing the inter-particle spacing) during the intermediate anneal.

To account for delayed recrystallisation in these alloys, Preston and Grant (134) postulated the pinning of deformation sub-cells, rather than recrystallisation nuclei pinning. (131). They proposed that the dispersion
of particles interferes with the migration of the sub-boundaries formed during deformation, in a manner analogous to the effect of particles on the mobility of high-angle boundaries (see section 1.4.7.4.).

Evidence has been produced which indicates that dispersion-strengthened alloys owe their excellent strength not only to the pinning of dislocations by particles but also to the trapped dislocations themselves. A thoria-dispersed nickel alloy only becomes fully resistant to softening at high temperatures if it is repeatedly strained and recovery-annealed (138). Each cycle re-arranges the dislocation distribution in such a way that resistance to recrystallisation is enhanced. It has been proposed (60) that this cyclic treatment reduces the inhomogeneity of the dislocation distribution. Recrystallisation will, therefore, be inhibited owing to the lack of regions having a significant lattice curvature (which is necessary for the formation of recrystallisation nuclei). Similar effects have been observed in copper-based alloys (128, 130). Humphreys and Martin (37) have observed a uniform dislocation arrangement in cold-worked copper alloys containing particles less than 0.3 microns in diameter. They reported that softening of these alloys occurred by recovery rather than recrystallisation.

Other work on thoria-dispersed nickel illustrates its resistance to recrystallisation. Von Heimendahl and Thomas (139) compared the annealing behaviour of pure nickel and thoria-dispersed nickel (with the particle diameter equal to 0.04 microns and the inter-particle spacing about a micron) after 90% deformation. Pure nickel fully recrystallises after one hour at 400°C, whereas thoria-dispersed nickel does not fully recrystallise even after an hour at 1200°C. Inman et al. (140) reported that the presence of thoria particles greatly reduces the nucleation rate of a 2 volume per cent thoria-nickel alloy compared with the solid-solution alloy. Webster (146) investigated the effect of prior deformation on the annealing characteristics of a similar alloy. He found that recrystallisation occurs above 675°C for material previously deformed by 87%. For deformations of 70% or less, recrystallisation begins at about 1200°C but is never completed at any temperature.

Brimhall et al. (142) have made a detailed study of the recrystallisation kinetics of internally oxidised silver-magnesium and copper-silicon alloys using transmission electron microscopy and hardness measurements. Some
of their results are shown in Figure 31. They proposed that the lack of recrystallisation is related to the nature of the sub-structure and the sub-grain boundaries in these alloys, implying that that resistance to recrystallisation is determined by the structure formed on deformation. They found that, on annealing, the generation of sub-grains from the cell structure formed during deformation is considerably more difficult for the materials containing dispersed particles than in similarly deformed single phase materials. In the silver-magnesia system, containing very fine dispersions (average particle diameter 0.005 μm and inter-particle spacing 0.05 μm), the small sub-grains formed on annealing are surrounded by low-angle boundaries. They suggested that annealing proceeds by the very slow growth of these sub-grains rather than the rapid migration of high-angle boundaries during conventional recrystallisation. In the copper-alumina alloy with a coarser dispersion (particle diameter 0.03 μm and inter-particle spacing 0.25 μm), the sub-grains are larger and are surrounded by higher angle boundaries. During annealing, some of the larger sub-grains eventually attain high-angle boundaries. However, recrystallisation is still appreciably retarded. Brimhall et al., therefore, postulated that, although the minimum size for recrystallisation nuclei formation is achieved, only low-angle boundaries surround the larger sub-grains and, consequently, the conditions for recrystallisation nuclei formation are not fulfilled. Humphreys and Martin (148) also suggested that, although the presence of a fine second phase hinders recrystallisation once it has begun, it is the deformed state which influences the recrystallisation characteristics of two-phase alloys.

The extreme case of metals containing a dispersed oxide phase is sintered aluminium powder (S.A.P.). This is a very stable material containing closely-spaced alumina particles. It has been reported that the resistance to recrystallisation of S.A.P. increases sharply with increasing alumina content (144, 145). Nobili et al. (145) have shown that the inhibition of recrystallisation gives an opportunity for the occurrence of recovery. They suggest that the role of the dispersed particles is to hinder high-angle grain boundary migration (needed for recrystallisation) and so permit recovery to occur. Increasing the alumina content makes recrystallisation even more difficult while recovery can still occur.
A number of studies have been made of the recrystallisation behaviour of alloys hardened by phases other than oxides. Detert and Ziebs (72) investigated the role of fine precipitates on the recrystallisation of nickel-tantalum-oxygen alloys. Although they did not know the composition of the precipitates, they found that the fine precipitates formed during annealing (i.e. after cold-working) at the sub-boundaries prevent the formation of nuclei and thus inhibit recrystallisation.

Ryum (141, 147) investigated the effect of precipitated $\text{Al}_3\text{Zr}$ particles on the plastic deformation and recrystallisation of an aluminium-zirconium alloy. Some of his results are shown in Figure 32. No dispersion parameters were given. The particles were distributed inhomogeneously in fan-shapes. He found the deformation structure in regions of high particle density to be decisively different from that in precipitate-free regions. The production of recrystallisation nuclei is never observed in the high particle density regions. He also found grain-boundary movement to be considerably hindered by the particles. He, therefore, attributed the increase in recrystallisation temperature to two causes: the change in the deformed structure due to the presence of the particles, and the pinning effect of the particles on the deformed structure and on the low- and high-angle grain boundaries. (See also this section).

Sundberg et al. (143) investigated the effect of silicon and zirconium on the recrystallisation behaviour of aluminium. Their alloys were heat-treated to give the solid-solution (super-saturated), fine and coarse precipitates, and were then deformed by 20, 50 and 90% reductions in thickness. The progress of recrystallisation was followed by hardness measurements and metallography. They found that the highest recrystallisation temperature is obtained with fine (0.05 microns), densely distributed, stable precipitates, zirconium being particularly outstanding in this respect. Large precipitates (of the order of a micron) reduced the recrystallisation temperature and produced the smallest as-recrystallised grain-size. The solid-solutions used for comparison purposes in this work were super-saturated versions of those alloys studied in the two-phase state. It would have been better to compare the behaviour of the dispersion alloys with that of the matrix phase of the two-phase structures.
Fig. 31. Hardness as a function of annealing temperature for silver-magnesia alloys, cold-rolled 75%.

Fig. 32. Hardness as a function of annealing temperature for △ super-pure Al, ○ Al-0.5%Zr solid-solution and ▼ Al-0.5%Zr dispersion alloy after 66% deformation.

Fig. 33. Apparent nucleation and growth rates as functions of time for 50% recrystallization for aluminium-copper alloys annealed at 305°C after 60% deformation.
There are several other papers, mainly Japanese work, dealing with the influence of zirconium on the annealing of aluminium. Most of them report that zirconium retards recrystallisation most strongly as finely dispersed precipitates. (See section 1.7.3.). However, the particle parameters were not quoted in any article.

Doherty and Martin analysed the recrystallisation of cold-worked aluminium-copper alloys both in polycrystalline (122) and monocrystalline (101) form. They showed that an alloy with an inter-particle spacing of 4 μm recrystallises at a much faster rate than that of a solid-solution alloy with the same matrix composition (Section 1.4.7.2.). However, reducing this spacing from 4 μm to 1.2 μm causes a drastic retardation of the recrystallisation process. The sizes of their particles were always less than 1 μm. They made approximate assessments of the rates of nucleation and growth, and plotted them as a function of the time for 50% recrystallisation (Figure 33). Doherty and Martin concluded that retarded recrystallisation is due to inhibited nucleation and not grain-boundary pinning. The variation of apparent nucleation rate with a parameter, R, is shown in Figure 19 for both polycrystalline and single crystal specimens (R is the radius of a sphere containing each particle and its associated solid-solution; it is proportional to the inter-particle spacing). It can be seen that for R values below 0.8 to 1.0 μm, the nucleation rate falls drastically. The increased rate of nucleation due to the presence of grain-boundaries can also be appreciated from this diagram. Doherty and Martin have suggested that this critical value of R corresponds to the critical size of a preformed nucleus. They proposed that, unless nuclei have become mobile before impingement on the second phase particles has occurred, nucleation will be very difficult and the recrystallisation process will be retarded.

Humphreys and Martin (128) investigated the effect of dispersed silica particles on the recrystallisation behaviour of deformed single crystals of copper. They confirmed Doherty and Martin's work that the same phase can accelerate or retard primary recrystallisation in a given system and that the decisive parameter is the inter-particle spacing. However, unlike Doherty and Martin, they reported that the apparent nucleation and growth rates of recrystallisation nuclei are both affected by comparable amounts with changes in inter-particle spacing. They interpreted this anomaly in
terms of a difference of interfacial energy between the silica particles and their matrix and the Cu Al$_2$ particles and their matrix. Mould and Cotterill (124), however, have shown that the apparent growth rates obtained by Doherty and Martin (122) do vary with inter-particle spacing. This is clearly illustrated in Figure 33.

Mould and Cotterill (124) further utilised Doherty and Martin's results (122) together with their own for dilute aluminium-iron alloys to postulate a model which could account for inhibited or accelerated recrystallisation in terms of sub-grain boundary pinning at or below a critical inter-particle spacing. They proposed that if the particle spacing is less than or equal to the sub-cell size after deformation, then recrystallisation delay will occur. Conversely, for coarse dispersions at spacings greater than the sub-cell size, accelerated recrystallisation is expected. Figure 35 shows their diagrammatic summary of the influence of degree of dispersion of a second phase on the recrystallisation behaviour of cold-worked metals.

Rollason and Martin (130) have recently studied the effect of particle size on the annealing behaviour of cold-worked copper-silica and aluminium-copper single crystals. They were mainly concerned with the effect of increased dislocation density due to the presence of particles on the nucleation stage of recrystallisation. They concluded that, for optimum, recrystallisation resistance in their alloys, the dispersed particles should have a diameter below the range 0.3 to 0.5 μm in order to suppress the development of local lattice curvatures on deformation. For effective resistance to recrystallisation, they suggested that dispersed particles of this diameter should be distributed at inter-particle spacings of not more than 1 μm.

1.4.7.4. Retardation of grain boundary migration by a fine dispersed phase.

The effect of finely dispersed particles on grain-boundary migration was first examined in connection with grain growth (Section 1.5). The fundamental theory has been presented by Smith (149) who followed an unpublished treatment by Zener.

Zener has shown that the maximum restraining force per unit area of boundary is given by
Fig. 34. Apparent nucleation and growth rates as a function of inter-particle spacing for aluminium-copper and aluminium-iron alloys.

Fig. 35. Schematic representation of the influence of degree of dispersion of a second-phase on the isochronal annealing behaviour of cold-worked aluminium alloys.
\[ F = n \pi r \phi \]  

where \( n \) = number of particles per unit area of grain boundary  
\( r \) = particle radius  
\( \phi \) = specific boundary interfacial energy (equivalent to a surface tension)

For random positioning of the grain boundary, the particle density is given by (150)

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

where \( f \) = volume fraction of particles

Substituting for \( n \) in equation (16) gives the maximum restraining force:

\[ F = \frac{3f \phi}{2r} \]

The assumptions made in deriving this equation are that the particles are uniform spheres randomly distributed, that the particle/matrix interfacial energy is independent of the matrix orientation, and that the grain boundaries are approximately plane and randomly positioned.

If the boundary is migrating entirely under the influence of its own interfacial tension and the grain periphery has a minimum radius of curvature, \( C \), then, the driving force for migration is given by \( \frac{2 \phi}{C} \).

For a homogeneous grain structure, \( C \) is approximately equal to the main grain diameter, \( D \). As grain growth occurs, \( D \) increases and the driving force diminishes. Eventually, a critical grain diameter is reached when the drag exerted by the particles balances the driving force. The critical grain diameter, \( D_c \), is then given by the condition

\[ F = \frac{2 \phi}{D_c} \]

Therefore, the critical grain diameter is found by substituting for \( F \) in equation (19):

\[ D_c = \frac{4r}{3f} \]
It is obvious from equation (20) that a given volume fraction of particles will be much more effective in limiting grain growth when the particle size is very small. In primary recrystallisation, where the driving force is much greater than $\frac{2\Phi}{C}$, the restraining effect due to particle drag will not be as effective (see section 1.4.7.3.).

A quantitative experimental verification of Zener's relation has not been made, although it is generally accepted as valid.
1.5. Grain Growth

When primary recrystallisation is complete, the grain structure of a metal is still not stable. Although the retained stored energy of cold-work has been spent, the metal can further approach stability by reducing the total surface area of its grain boundaries. Therefore, during grain growth the number of grains decreases, the grain boundary area diminishes and the total surface energy is lowered accordingly. The detailed grain morphologies produced during grain growth have been discussed by McLean (55).

As the growth of cells in a foam of soap bubbles also occurs as a result of a decrease in surface energy, such froths have been used as a quantitative analogy for an unstable grain structure (149). In a soap-bubble array, it has been experimentally confirmed (151) that the bubble diameter, \( D \), follows a time law, as follows:

\[
\frac{dD}{dt} = \frac{1}{D} \tag{21}
\]

This law follows directly from the hypothesis that the rate of boundary migration is inversely proportional to the mean radius of curvature, and that this in turn is proportional to \( D \). Integration of equation (21) leads to the expression

\[
D^2 - D_0^2 = kt \tag{22}
\]

where \( D_0 \) = size of average cell when \( t = 0 \)

\( k \) = constant

Assuming that \( D_0^2 \) can be neglected compared with \( D^2 \), the ideal grain growth law can be stated in the simpler form

\[
D = k t^{\frac{1}{2}} \tag{23}
\]

Experimental grain growth data for a number of pure metals correspond to empirical equations of the form

\[
D = k t^n \tag{24}
\]

where the grain growth exponent, \( n \), is, in most cases, smaller than the value predicted by equation (23). Also, Fullman (151) has shown that \( n \) is not constant for a given metal or alloy, if the isothermal reaction temperature is changed. The exponent increases with increasing temperature, tending towards the
The grain growth law (equation 23) can be disturbed by a number of factors. In particular, solid solution impurities slow down and may eventually stop grain-growth. This has been dealt with in section 1.4.6.2.3.

A dispersed phase can also retard boundary motion and bring grain growth to a halt. (See section 1.4.7.4.). Beck et al. (168) studied the effect of particles on grain growth in an aluminium - 1.1% manganese alloy. The Mn Al_6 particles in this alloy exist up to 625°C, but dissolve above 650°C. At 625°C and below, grain growth is almost completely stopped (n ~ 0.02). However, at 650°C, grain growth proceeds very rapidly, with n approaching the theoretical value.

It can be concluded that the retarding effect of impurities, whether in solid-solution or as second phase particles, on boundary migration is reduced as the temperature is increased, and grain growth then occurs under conditions closely resembling the growth of soap cells.
1.6 Summary

The prior history of metals governs to a great extent their recrystallisation behaviour. The amount, nature and temperature of deformation all affect the cold-worked structure, which in turn influences recrystallisation. The extent of recovery also affects recrystallisation.

The main points and factors concerning the annealing of cold-worked metals will now be outlined.

(a) Recrystallisation is a two-stage process of nucleation and growth.
(b) Several nucleation mechanisms have been proposed.
(c) The growth of recrystallisation nuclei occurs by the migration of high-angle boundaries through the deformed structure.
(d) When the recrystallisation nuclei have completely occupied the deformed structure, primary recrystallisation is completed.
(e) Grain growth occurs after primary recrystallisation.
(f) Solid-solution elements affect the formation of a sub-grain structure during deformation.
(g) Solid-solution impurities decrease grain-boundary mobility during annealing.
(h) Second-phase particles influence the formation of a sub-grain structure during deformation.
(i) Second-phase particles affect the migration of low- and high-angle boundaries during annealing.
(j) The size and spacing of second-phase particles affect the rate of recrystallisation.
1.7. The present work

1.7.1. Objectives

Two different technological aspects of the annealing behaviour of cold-worked metals are of interest. In some cases, a material which recrystallises easily and, therefore, produces a fine grain-size is required. In other instances, a material with the highest possible recrystallisation temperature is needed in order to increase the temperature range over which the increased strength due to cold-work can be retained. In any event, it is necessary to have knowledge of the recrystallisation temperature range because:

(a) it denotes the maximum service temperatures for work-hardened metals;
and (b) it signifies the minimum temperature at which hot working can be carried out.

Although the information outlined in the literature survey has shown the possibilities of retarded or accelerated recrystallisation as a function of particle size and spacing, these modes of behaviour have not been widely studied within any one alloy system. In general, previous correlations have been made by comparing different sets of work in different alloy systems. The present work, therefore, was initiated to study the role of second-phase particles on the transition from accelerated to retarded recrystallisation, and to gain more information concerning the influence of initial grain-size and amount of prior deformation.

1.7.2. Selection of alloy system

The choice of alloy system is governed by the objectives outlined in section 1.7.1. For this type of investigation, the important requirements of an alloy system are the ability to produce a range of particle sizes and spacings, and particle and matrix stability.

There are several ways in which dispersion alloys can be produced.

(i) By the precipitation of particles from a super-saturated solid-solution. Recrystallisation characteristics can be studied when the second-phase particles are fully incoherent. The particles are then very fine and very
closely spaced. (For example, the work of Doherty and Martin (122).)

However, unless recrystallisation occurs below the over-ageing
temperature, annealing for constant times at different temperatures
produces a variable solid-solution composition, particle size and
particle density. It is also difficult to obtain coarse, widely-spaced
particles.

(ii) By the hot-working of as-cast structures

The second-phase must be a very hard and stable intermetallic compound,
the solid-solubility of which must decrease very rapidly with decreasing
temperature and approach zero at as high a temperature as possible.
The as-cast eutectic or peritectic structure has to be broken down to
produce an even distribution of coarse, very stable particles. (For
example, the work of Mould and Cotterill (124).) The use of such alloys
enables isochronal annealing to be employed for recrystallisation studies.

(iii) By powder metallurgy or the internal oxidation of alloys

Powder metallurgy is used to produce dispersion alloys by compacting,
hot pressing and extruding a mixture of finely divided metal powders and
oxide or intermetallic compound powders. (For example, the work of
Nobili et al. (145).)

Dispersions of a finely divided oxide in a metal matrix can also be
produced by the internal oxidation of alloys in which the solute metal
forms a more stable oxide than the solvent metal, and in which the solvent
metal has an appreciable affinity for oxygen. The alloys may be internally
oxidised as sheet or wire, or in the form of powder which is consolidated
by powder metallurgy methods. (For example, the work of Humphreys and
Martin (128).) However, different particle sizes are produced, resulting
in non-uniform particle spacings. The recrystallisation temperature
range can also be investigated by means of isochronal annealing.

It was decided to use a two-phase aluminium binary system which would
lend itself to the production of dispersions by methods (i) [for closely-spaced,
fine particles] and (ii) [for widely-spaced, coarse particles]. Figure 36
and Table 1 indicate that the use of a peritectic system may be more
advantageous than a eutectic system for recrystallisation studies. In
particular, Figure 36 shows that the amount of second-phase desired can be achieved more accurately in a peritectic system as the solute range is much longer. Also, the sluggishness of the peritectic reaction enhances the formation of a super-saturated solid-solution under very fast cooling conditions.

Therefore, it was decided to use a peritectic alloy system, and the system aluminium-zirconium was adopted. Forging was selected as the most favourable method for breaking down as-cast structures because a more uniform deformation distribution is created than in rolling or extrusion.

The purpose of this investigation is, therefore, to examine the influence of zirconium on the recrystallisation of aluminium in an attempt to clarify the conditions which cause recrystallisation to be accelerated or retarded. The variables are the alloy composition, initial grain-size, amount of prior deformation, and the particle size and distribution.

1.7.3. The characteristics of the aluminium-zirconium system

Dilute aluminium-zirconium alloys undergo a peritectic type of reaction at 660.5°C between the melt containing 0.11 wt.% Zr and Al$_3$Zr to form an aluminium-rich solid-solution containing a maximum of 0.28 wt.% Zr. The solid-solubility of zirconium in aluminium decreases with falling temperature to about 0.05 wt.% Zr at 500°C (152). The relevant portion of the equilibrium diagram is shown in Figure 37.

The zirconium-rich constituent, Al$_3$Zr, consists of very stable body-centred tetragonal crystals of structure type DO$_{23}$ and lattice parameters of $a = 4.013 \, \AA$ and $c = 17.32 \, \AA$ (152, 153). Pearson (154) quotes the experimentally measured density of single crystals of Al$_3$Zr as 4.11 gms/cc. The same figure has also been obtained by calculations based on X-ray measurements.

The annealing behaviour of various aluminium-zirconium alloys has been studied by several workers, with partially contradictory results. Particle size and density have only been quoted by Sundberg et al. (143). It has mostly been reported that zirconium retards recrystallisation most strongly as finely dispersed precipitates. Quantitative values of the recrystallisation temperature of aluminium when influenced by zirconium
Table 1. Data for aluminium alloys which show negligible solid-solubility of an inter-metallic compound. Collated from Hansen (166)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>wt% solute</th>
<th>wt% solute</th>
<th>temp. °C</th>
<th>wt% solute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Co</td>
<td>-</td>
<td>0.02</td>
<td>1.0</td>
<td>Co$_2$Al$_3$</td>
</tr>
<tr>
<td>Al-Fe</td>
<td>0.006</td>
<td>0.05</td>
<td>1.7</td>
<td>FeAl$_2$</td>
</tr>
<tr>
<td>Al-Ni</td>
<td>0.006</td>
<td>0.05</td>
<td>5.7</td>
<td>NiAl$_2$</td>
</tr>
<tr>
<td>Al-Ti</td>
<td>0.24</td>
<td>1.15</td>
<td>6.7</td>
<td>TiAl$_2$</td>
</tr>
<tr>
<td>Al-Zr</td>
<td>0.05</td>
<td>0.28</td>
<td>6.6</td>
<td>ZrAl$_2$</td>
</tr>
</tbody>
</table>

Fig. 36. Schematic comparison of eutectic and peritectic systems of aluminium alloys which show negligible solid-solubility of an inter-metallic compound.

Fig. 37. The aluminium-zirconium equilibrium diagram.
additions have been obtained from the literature and are shown in Figure 38 and Table 2.

Yamada (155) has reported that 0.25% Zr has the same retarding effect on aluminium whether in solid-solution or as fine precipitates. However, 0.45 wt. % Zr as fine precipitates has a much greater effect than the same amount in solid-solution.

The work of Araki and Komori (156-158) is somewhat confusing. In one paper, they report that precipitation heat-treatment at 500°C before deformation does not alter the recrystallisation temperature compared with the equivalent solid-solution (156). In other papers, they indicate that a heat-treatment at 450°C or 500°C before deformation (158) or one at 300°C after deformation (157) elevates the recrystallisation temperature compared with the solid-solution.

Nishikawa et al. (159) have reported that 0.15 to 0.2 wt. % Zr considerably raises the recrystallisation temperature of aluminium. They have also shown that 0.3 wt. % Zr as fine precipitates has a greater retarding effect than the same amount of zirconium in solid-solution (160). Further results indicate that, after precipitation heat-treatments at different temperatures, the material which ought to have the largest precipitates, has the lowest recrystallisation temperature (161).

Ryum (141, 147) found that, after a heat-treatment at 500°C, 0.5 wt. % Zr impedes recrystallisation far more as the fine transitional precipitates than as the same amount in solid-solution.

The work of Sundberg et al. (143) shows that, for a 0.3 wt. % Zr alloy, "coarse" precipitates (0.2 μm), produced by a heat-treatment at 500°C, accelerate recrystallisation whereas "fine" precipitates (0.1 μm), produced by a heat-treatment at 400°C, retard the recrystallisation process compared with the equivalent solid-solution. They also report that 0.63 wt. % Zr, when present as fine precipitates after a heat-treatment at 400°C, has a greater retarding effect than the same amount in solid-solution.
Fig. 38. 50% softening temperatures as a function of percent Zr and precipitation conditions.

Table 2. Values of 50% softening temperature for several aluminium-zirconium alloys after various heat-treatments, amounts of deformation and times of annealing.
2. EXPERIMENTAL TECHNIQUES

2.1 Introduction

Eleven alloys were investigated, ten of which were two-phase structures containing stable $\text{Al}_3\text{Zr}$ particles dispersed within a constant composition aluminium-zirconium solid-solution. Hardness and metallography were used to examine the recrystallisation characteristics of these alloys as a function of their composition, particle size and distribution, matrix grain-size as well as the amount of prior deformation.

The alloys were prepared by melting selected quantities of aluminium and zirconium. Relatively coarse dispersions were produced by forging specimens having two-phase, as-cast, peritectic structures. Finer dispersions were obtained by the precipitation of $\text{Al}_3\text{Zr}$ particles within specimens cast as super-saturated solid-solutions. A carefully devised combination of deformation and annealing treatments was then used to complete the homogenisation of the particle distribution, and to produce controlled variations in the matrix grain-size, under conditions which lead to a constant solute content in the matrix of all the two-phase alloys.

Typical samples were examined metallographically at each stage in the specimen production sequence, and their final constitution and structure were assessed by a combination of chemical analysis, X-ray analysis and quantitative metallography.

The overall sequence of experimental procedures is indicated in Figure 39, and the individual techniques are described, in detail, in the following sections.
Fig. 39. Flow sheet of experimental techniques.
2.2. Specimen preparation

2.2.1. Materials

The material used as a base for the production of all the alloys was super-pure aluminium. This was supplied by the British Aluminium Co. Ltd., who gave the specification as 0.0026 wt.% Fe, 0.0065 wt.% Si and 0.0005 wt.% Cu. The zirconium (purity 99.8%) was supplied in the form of sponge pellets (2 to 12 mm) by Metals Research Ltd.

2.2.2. Casting

2.2.2.1. Alloys with a two-phase as-cast structure

Preliminary experiments revealed that the preparation of these alloys required great care. Initially, melts were chill-cast into a rectangular mild steel mould of dimensions 10 cms length x 5 cms width x 15 cms height. However, this produced an uneven distribution of the second-phase. It was decided to improve the distribution by increasing the solidification rate of the castings. This was done by water-cooling the same mould. Better structures were only achieved for low zirconium contents only. A faster cooling rate was obtained by chill-casting the alloys into a vertical cylindrical mild steel mould of dimensions 21 cms height by 4.7 cms internal diameter. A uniform distribution of Al$_3$Zr plates throughout the castings was obtained. This method was, therefore, adopted.

The alloys were melted in a gas-fired furnace using plumbago crucibles. The addition of zirconium pellets to the molten aluminium took place under a cover of charcoal. The melt was then stirred with dry graphite rods to ensure good mixing of the two metals.

Each melt was given two degassing treatments, using "Foseco degasser 190". The first treatment took place just before the introduction of the zirconium pellets. The melts were finally degassed before pouring. Then, they were cast into the mould from a temperature just above the liquidus of the particular alloy being prepared. High casting temperatures were necessitated by the high liquidus of the system.
A primary pipe was present in each ingot to a depth of \( \sim 2 \) cms. Therefore, the top 3 cms of all the ingots were removed, and the remaining cast-surfaces were ground to remove any surface defects and oxide skin. Each prepared ingot yielded a minimum of six blocks of dimensions 2.5 cm width x 2.5 cm thickness x 3.8 cm length. Metallographic examination revealed an even distribution of \( \text{Al}_3\text{Zr} \) plates throughout the blocks, which were then ready for the forging treatment.

### 2.2.2.2. Alloys with a super-saturated solid-solution structure

A preliminary experiment revealed that very rapid solidification of an alloy of this system caused the peritectic reaction to be suppressed with the resultant formation of a super-saturated solid-solution. Further heat-treatment at a temperature just below the peritectic horizontal for ageing times in excess of 120 hours produced an even distribution of fine \( \text{Al}_3\text{Zr} \) particles. This method was, therefore, used to produce three alloys.

These alloys were melted and degassed exactly as outlined in section 2.2.2.1. However, they were chill-cast into a cylindrical copper mould set in an aluminium block. The mould was of the dimensions 22 cms height x 1.2 cms internal diameter. It had a wall thickness of 1.6 cms and the surrounding aluminium block had a thickness of 4 cms.

Each ingot was machined to give flat edges, and was then ready for the ageing treatment.

### 2.2.3. Production of homogeneous dispersions

#### 2.2.3.1. Forging of two-phase alloys

A preliminary experiment indicated that the best structure for these alloys was obtained by initially cold-forging the ingot blocks, followed by a hot-forging sequence carried out at a maximum temperature of 630°C. During cold-forging, the blocks were axially compressed through their longest dimension until an equivalent radial expansion was produced. This was done for 5 passes, and the blocks were rotated through 90° between each pass.

The first stage of the hot-forging sequence consisted of the same treatment carried out during cold-forging. In the final stage of hot-forging, the blocks
were axially compressed into the shape of a boat (thickness 1.3 cm) which was then forged through its width until a strip of dimensions \( \sim 31 \text{ cms length } \times 1.3 \text{ cms width } \times 0.65 \text{ cms thickness} \) was produced. The hot-forging sequence consisted of 20 passes, and the blocks were reheated to the forging temperature and rotated through 90° between each pass.

The forging operation can be summarised as follows:

**Cold-forging:** From 3.8 cms to 1.95 cms for 5 passes  
**Hot-forging:** From 3.8 cms to 1.95 cms for 5 passes  
From 1.95 cms to 1.3 cms for 5 passes  
From 1.3 cms to 0.98 cms for 5 passes  
From 0.98 cms to 0.65 cms for 5 passes

A total of 25 passes was used.

Metallographic examination indicated that second-phase particles were evenly distributed throughout the strips. 4 cms were removed from each end of the strips which were then lightly ground to give parallel sides. The strips were then ready for further treatments.

### 2.2.3.2. Precipitation from super-saturated solid-solution alloys

A preliminary experiment indicated that the second phase was precipitated after long annealing times (\( \geq 80 \) hours) at 600°C. This is in agreement with the work of Ryum (147), who reported that tetragonal \( \text{Al}_3 \text{Zr} \) particles appeared after 120 hours at 500°C.

Therefore, the machined slabs from the casting stage were lightly cold-rolled (15% reduction in thickness) and fully aged at 630°C for 170 hours, followed by furnace cooling. These strips were then available for the subsequent experiments.

### 2.2.4. Standardisation of matrix-phase

#### 2.2.4.1. Solute content

A cold-rolling treatment was given to the strips from all the alloys. This was followed by a recrystallisation anneal at 450°C for 48 hours for the dispersion alloys and 2 hours for the solid-solution alloy and super-pure
aluminium. This heat-treatment ensured that the solute content of the matrix in all the two-phase alloys was equal to the equilibrium solubility limit at 450°C. After water-quenching from 450°C, the strips were then ready for the final cold-rolling and annealing treatments.

2.2.4.2. Grain-size

For all the alloys, the effect of deformation on grain-size after annealing at 450°C was determined. This was done by varying the degree of the cold-rolling treatment during the intermediate process performed to standardise the solid-solution content (as described in section 2.2.4.1.), and measuring the resultant grain-size.

From the plots of grain-size against deformation, the amount of cold-work required to produce a constant original grain-size of 0.08 mm in each of the two-phase alloys was determined. This deformation was then applied to the strips during the intermediate treatment. In such a way, the same initial grain-size could be produced in all the two-phase alloys.

Three alloys were selected to investigate the effect of original grain-size on recrystallisation. These were a solid-solution alloy (0.02 wt. % Zr) and two dispersion alloys (1.30 % Zr and 9.18 % Zr). A grain-size variation was achieved in each alloy by varying the degree of deformation carried out during the intermediate treatment.
2.3. Specimen assessment

2.3.1. Constitution

2.3.1.1. Composition

Samples from each alloy were analysed by Acloque (Metallurgists) Ltd. for zirconium, iron and silicon. They were degreased and lightly pickled prior to analysis.

2.3.1.2. Phase analysis

The Debye-Scherrer powder-diffraction method was used to identify the phases present in two alloys, 1.10% and 6.97% Zr. Samples from each alloy were filed to a powder. Unfiltered copper radiation was used. The films were analysed by means of a 'd'-spacing ruler, and the values obtained were compared with those given in the ASTM Index. (Card No. Z - 1093).

2.3.2. Metallography

2.3.2.1. Specimen preparation

This section deals with the techniques by which specimens were prepared and examined.

2.3.2.1.1. Optical microscopy

Specimens for metallographic examination were ground through successively finer grades of silicon carbide paper, using water as lubricant and coolant. They were then given a final polishing on polishing cloths impregnated with 6 μ, and, lastly, 1 μ diamond polishing compound. Specimens were then given a short (1 minute) electro-polishing treatment in a solution of 5% perchloric acid - glacial acetic acid using an aluminium cathode. A voltage of 18 volts was applied and stirring at about 100 revolutions per minute was used. The specimens were immersed in water immediately after the electro-polishing operation.

In the as-polished condition, Al₃Zr particles were easily discernible and appeared light-grey. None of the standard reagents used to identify constituents in aluminium alloys caused any alteration in them.
For further metallographic examination, specimens were prepared by electrolytic etching. The best results were obtained when an anodising solution of 5\% hydrofluoroboric acid in distilled water was used at a potential of about 22 volts for three minutes. A carbon cathode was used. This method produced an oxide film which gave good grain contrast when viewed under polarised light. Grain boundaries could also be clearly observed when viewed under "normal light" conditions.

### 2.3.2.1.2. Electron (stereoscan) microscopy

Conventional microscopic examination of all the alloys in the as-polished condition indicated that the particle shape could not be approximated to spheres, as is normally the case in recrystallisation studies. Scanning electron microscopy was, therefore, utilised to determine the true shape of the particles.

Samples from every alloy were immersed in a normal solution of caustic soda. This partially dissolved the matrix without attacking the Al\textsubscript{3}Zr particles. After washing and drying, the specimens were examined in a Cambridge "Stereoscan" Mark IIA at magnifications in the range x600 to x6000.

### 2.3.2.2. Quantitative metallography

#### 2.3.2.2.1. Matrix grain-size

The grain-size was determined by a lineal intercept method, using the number of grain boundaries crossed in a known distance to calculate the average grain diameter. For all worked specimens, the grain-size was measured in a section perpendicular to the working direction. The number of grain boundaries crossed were counted in a single traverse from one edge of the specimen to the other. This was checked by reversing the direction of traverse. The determination was carried out on a movable microscope stage so that the traverse distance could be accurately measured. Counts were made for five traverses across the widths of the specimens, and three traverses across their thicknesses. An average of these results gave the final grain-size.
2.3.2.2.2. Particle shape

Certain characteristics applicable to systems of particles in a matrix can be measured exactly without any special assumptions; for example, the volume fraction and the mean free path. Other properties, including nearest-neighbour distances (e.g. $\Delta_3$) cannot be obtained rigourously, particularly when the shape of the particles must be specified. In these cases, it is necessary to approximate the true particle shape to some geometrical figure, and base any calculations on this approximation.

In the present work, optical microscopy and stereoscan observations indicate that the real particles of Al$_3$Zr can be approximated to the ideal shape of a square plate for the purpose of further calculations (See Figures 41 and 42).

2.3.2.2.3. Particle distribution

Particle counting was carried out on two specimens for each alloy. The specimens were transverse sections taken from the strips which had had the solid-solution standardisation treatment. They were polished as outlined in section 2.3.2.1.

For $N_a$ determinations, the specimens were examined on a Zeiss Ultraphot II photomicroscope at magnifications in the range x277 to x1038. Several photographs were taken at random positions of each specimen. The number of particles was counted on each photograph. An average value was obtained to give the number of particles per unit area.

$N_L$ was determined by a lineal intercept method, similar to the one outlined in section 2.3.2.2.1., using the number of particles intercepted in a known distance. The determination was carried out on a microscope with a travelling stage attachment. A magnification of x600 was used. Counts were made for 5 traverses across the widths of the specimens, 3 across their thickness, and 1 traverse along each diagonal. An average of these results gave the final value for $N_L$. 
2.3.2.4. Particle size

By assuming that the real particles approximate to the ideal shape of a square plate, there exist exact relationships which yield the true dimensions of the particles (162):

\[ a = \frac{2N_L}{N_A} \]  \hspace{2cm} \ldots(25)

and  \[ 2t = L_3 = \frac{1}{N_L} \]  \hspace{2cm} \ldots(26)

where 'a' is the edge and 't' is the thickness, and 'a' is much greater than 't'.

Therefore, by determining the number of particles in a plane of polish, \( N_A \), and the number of particles intercepted in a unit length of test line, \( N_L \), the true particle dimensions can be calculated. The values obtained can be compared with the results obtained from measurements on the stereoscan prints.

2.3.2.5. Particle volume fraction

The volume fraction of dispersed particles can be calculated theoretically from the Al-Zr equilibrium diagram, using the following information:

(a) composition of the alloy = x wt.% Zr

(b) composition of the solid-solution at 450°C = 0.03 wt. % Zr
(by extrapolating Fink and Willey's results (152))

(c) density of the solid-solution
= 2.70 gm/cc
(Smithells (165))

(d) composition of \( Al_3Zr \)
(Hansen (166))
= 52.99 wt.% Zr

(e) density of \( Al_3Zr \)
(Pearson (154))
= 4.11 gm/cc

The volume of \( Al_3Zr \) is given by

\[ \frac{x - 0.03}{52.99 - 0.03} \times \frac{1}{4.11} \]

and the volume of solid-solution is

\[ \frac{52.99 - x}{52.99 - 0.03} \times \frac{1}{2.70} \]

Therefore, the volume fraction is equal to

\[ F_V = \frac{2.70 (x - 0.03)}{2.70 (x - 0.03) + 4.11 (52.99 - x)} \]  \hspace{2cm} \ldots(27)
2.3.2.6. Inter-particle spacings

The mean-free path, $\lambda$, as defined by Fullman (163) is valid regardless of the size, shape or distribution of particles. It is given by

$$\lambda = \frac{1 - F_v}{N_L}$$

...(28)

This spacing represents the uninterrupted inter-particle distance through the matrix averaged between all possible pairs of particles. It is essentially a mean edge-to-edge distance.

The mean random spacing, $\sigma$, represents the mean uninterrupted centre-to-centre length between all possible pairs of particles, and is equal to the reciprocal of $N_L$. Also, the difference between $\sigma$ and $\lambda$ gives $L_3$.

Therefore, by knowing $F_V$ and $N_L$, the mean free path and the mean random spacing can be determined.

Two precisely defined nearest-neighbour distances are known. They are denoted by $\Delta_3$ and $\Delta_2$, and are defined as the average centre-to-centre distance between any particle and its nearest neighbour in a random distribution of particles, in a volume and in a plane respectively. Gurland (164) has given formulae for these distances.

$\Delta_3$ is derived as follows:

The probability that a particle exists within the spherical shell between $R$ and $R + dR$ is

$$P(R) dR = \left[1 - \int_0^R P(R) dR\right] 4\pi R^2 N_V \cdot dR \quad \ldots(29)$$

The function that satisfies equation (29) is found to be

$$P(R) = 4\pi R^2 N_V \cdot e^{-\frac{4}{3}\pi R^3 N_V} \quad \ldots(30)$$

$N_V$ is the number of particles per unit volume. By definition,

$$\Delta_3 = \int_0^\infty R \cdot P(R) dR \quad \ldots(31)$$

Substituting equation (30) into equation (31) and integrating, the following
The equation is obtained

\[ \Delta_3 = 0.554 N_V \]

\[ \Delta_3 = 0.554 N_V \]

\[ \text{(32)} \]

For particles conforming to the shape of a square plate,

\[ N_V = \frac{N_A^2}{2N_L} \]

\[ N_V = \frac{N_A^2}{2N_L} \]

\[ \text{(33)} \]

Consequently, \( \Delta_3 \) can be determined. A similar derivation gives the following result for \( \Delta_2 \):

\[ \Delta_2 = 0.5 N_A^{-\frac{1}{2}} \]

\[ \Delta_2 = 0.5 N_A^{-\frac{1}{2}} \]

\[ \text{(34)} \]

Therefore, knowledge of \( N_L \) and \( N_A \) gives directly values for \( \Delta_3 \) and \( \Delta_2 \).
2.4 Study of recrystallisation characteristics

2.4.1. Deformation

All the alloys were given their final amount of cold deformation (10, 30 or 60% reduction in thickness) in a two-high mill with 15 cms diameter rolls. A series of passes was used to obtain the required final thickness. A reduction per pass of 0.25 mm was aimed at until the strip thickness approached the final value. Then, smaller reductions were applied.

The rolling speed was always low enough to prevent the temperature of any strip rising.

The cold-rolled strips were cut into several specimens, \( \sim 1.5 \text{ cm x 1.5 cm} \). Their sawn edges were lightly ground to remove any heavy localised deformation before the final annealing treatments were carried out.

2.4.2. Annealing

2.4.2.1. Isochronal annealing

Specimens were given annealing treatments of one hour at temperatures in the range 100°C to 500°C. The furnaces used for the heat-treatments were as follows:

(a) Oil-bath, with a means for circulating the oil. The oil was heated by an immersion element. The accuracy of the furnace was \( \pm 3^\circ \text{C} \), and it was used in the temperature range, 100°C to 200°C.

(b) Salt-bath. A bath of "Cassel TS 150" salt was regulated by means of a Eurotherm thyristor temperature controller. The furnace, which was accurate to \( \pm 1^\circ \text{C} \), was used in the temperature range, 200°C to 500°C.

After being held at temperature for one hour, the specimens were immediately quenched into water.

2.4.2.2. Isothermal annealing

Specimens were isothermally annealed in the salt-bath furnace at temperatures of 335°C and 375°C. The time of annealing was measured from the moment
the specimens were immersed into the bath until their removal. After annealing, the specimens were water-quenched.

2.4.3. Assessment of recrystallisation

2.4.3.1. Macrohardness measurements

Specimens for hardness testing were ground until approximately one-third of their surface was removed, and then polished to a one micron diamond finish.

Vickers hardness values were determined using a load of 2.5 kilograms and an objective lens of 17 mm focal length. Indentations were made evenly across the surface of each specimen parallel to the direction of rolling. Eight impressions were made on every specimen, and the mean value and the standard deviation from it were calculated.

The "rate of change" technique devised by Mould and Cotterill (124) for the assessment of hardness data has been outlined in section 1.4.1.2., and has been used in the present investigation. The temperature (or time) at which the rate of change of hardness is a maximum was taken as the temperature (or time) corresponding to 50% recrystallisation. The temperature (or time) at which the rate of change decreases to zero after recrystallisation gave the temperature (or time) of the completion of recrystallisation. Figure 47 illustrates the use of this technique for super-pure aluminium and an Al - 0.02 % Zr solid-solution alloy.

2.4.3.2. Metallography

The progress of recrystallisation was followed metallographically using a point-counting procedure. This entailed counting the proportion of 100 intersection points occupied by recrystallised grains. The intersection points formed a total of 8 cms x 11 cms on the screen of a Zeiss Ultraphot II photomicroscope. A constant magnification of x104 was used, and several areas were selected to furnish a final average value. Any specimen which had an average of 50 intersection points occupied by new grains was considered to be 50% recrystallised.
The first isochronally annealed specimen to reveal the presence of new grains was taken as the temperature at which recrystallisation began. The specimen heated to the lowest temperature (or for the shortest time) to produce a completely recrystallised structure was considered to be the temperature (or time) at which recrystallisation ended.

Metallography, therefore, served to check the recrystallisation temperatures and times determined from the hardness data. The point-counting method used in the present investigation was tedious, and was impossible to use on specimens which had recrystallised by more than 60%. At lower recrystallised fractions, the good grain contrast obtained by electro-polishing and electrolytic etching permitted accurate assessments of the amount of recrystallisation to be made.

Estimates of the apparent nucleation rate, \( \dot{N}' \), and the apparent growth rate, \( \dot{G}' \), were made by using the following formulae (122):

\[
\dot{N}' = \frac{\text{number of grains per cubic millimetre}}{\text{time for 100% recrystallisation}}
\]

therefore \( \dot{N}' = \frac{3}{4\pi r^3 \times t_c} \)  \( \quad \ldots \) (35)

and \( \dot{G}' = \frac{\text{average radius of recrystallised grains}}{\text{time for complete recrystallisation}} \)

therefore \( \dot{G}' = \frac{r}{t_c} \)  \( \quad \ldots \) (36)

By assuming that each recrystallised grain is a sphere, the true radius \( r \) can be calculated from the measured grain-size values, which are equal to \( \frac{4}{3} \).

The value \( \dot{N}' \) assumes that each recrystallised grain has resulted from one nucleus, so that the final number of grains is related to the number of nuclei. Also, the value \( \dot{G}' \) depends on the grain-size being related to the growth rate of the nuclei.

As the values make no allowance for
(i) the impingement of neighbouring grains, and
(ii) the possibility of some grain growth before recrystallisation is complete, they must be taken as only approximate indications of the conventional nucleation
and growth rates. However, they are not seriously in error for comparative purposes.
3. RESULTS

3.1. Alloy characteristics

3.1.1. Composition

The results of the chemical analysis are presented in Table 3. For every alloy, the amount of iron was less than 0.03 wt. %. The letters designated to the alloys were used for convenience during the investigation.

3.1.2. Phase identification

Figure 40 shows the Debye-Scherrer powder diffraction photographs for two alloys, Al - 1.10 % Zr and Al - 6.97 % Zr. The patterns are adequate for the identification of the phases present in the alloys, using the ASTM index cards for Al, Zr and Al. Unaccountable lines were attributed to the presence of alumina and/or zirconia in the samples.

3.1.3. Dispersion data

Details of the various dispersion characteristics (i.e. volume fraction, number and size of particles, and various particle-spacings) are given in Table 4.

The metallographic appearance of the alloys is shown in Figure 41. Corresponding stereoscan photomicrographs are presented in Figure 42.

3.1.4. Matrix grain-size

Figure 43 illustrates the effect of different amounts of deformation during the intermediate treatment (used to standardise the solid-solution content) on the resultant grain-size for all the alloys. Photomicrographs of several of the alloys after this treatment are shown in Figure 44.

Table 5 indicates the amounts of deformation which were estimated as being required during the intermediate treatment in order to achieve an initial grain-size of 0.080 mm on the basis of the data presented in Figure 43. Also tabulated are the grain-sizes actually obtained.
3.2. Deformation and annealing characteristics

3.2.1. Deformation

Figure 45 presents the structure of several of the two-phase alloys after the final amount of deformation. The effect of the final deformation on the hardness of some of the alloys is shown in Figure 46.

3.2.2. Isochronal annealing

3.2.2.1. The effect of zirconium in solid-solution

Figure 47 presents the hardness results for super-pure aluminium and an Al - 0.02 % Zr solid-solution alloy, which have similar initial grain-sizes, plotted against temperature. This diagram also illustrates the "rate of change" technique described in section 1.4.1.2.

The variation of hardness with annealing temperature after 30% and 60% deformation is shown in Figure 48 for the Al - 0.02 % Zr solid-solution alloy with different initial grain-sizes.

Figure 49 illustrates the effect of initial grain-size on the recrystallisation temperatures after 30% and 60% deformation. \( T_C = \text{the finish of recrystallisation} \), \( T_{1/2} = 50\% \text{ recrystallisation} \), \( S_1 = 50\% \text{ softening} \), and \( T_S = \text{the start of recrystallisation} \).

The dependence of the as-recrystallised grain-size on the original grain-size is shown in Figure 50.

3.2.2.2. The effect of the matrix grain-size in two-phase alloys

The variation of hardness with annealing temperature, and the effect of different initial grain-sizes, are presented in Figure 51 for Al - 1.10 % Zr, Al - 1.30 % Zr and 9.18 % Zr alloys, after 60% deformation.

The dependence of the recrystallisation temperatures on initial grain-size is shown in Figure 52 for these alloys.

Figure 53 illustrates the variation of as-recrystallised grain-size with original grain-size for Al - 1.10 % Zr, Al - 1.30 % Zr, Al - 6.97 % Zr and Al - 9.18 % Zr alloys after 60% deformation.
3.2.2.3. The effect of the amount of prior deformation in two-phase alloys

The change in hardness with annealing temperature is shown in Figure 54 for all two-phase alloys after 10, 30 and 60% deformation. Table 6 collates the relevant data from Figure 54.

The dependence of the recrystallisation temperatures on inter-particle spacing is illustrated in Figure 55 for each deformation.

Figure 56 shows the variation of the as-recrystallised grain-size with inter-particle spacing for each deformation.

The effect of the final amount of deformation on the 50% recrystallisation temperature and fully recrystallised grain-size is shown in Figures 57 and 58.

3.2.3. Isothermal annealing at 335°C

3.2.3.1. The effect of zirconium in solid-solution

The change in hardness with time of annealing after 30% and 60% deformation is presented in Figure 59 for the Al - 0.02% Zr solid-solution alloy with different original grain-sizes. Table 7 collates the data obtained from Figure 59.

The dependence of the recrystallisation times (i.e. $t_\frac{1}{2}$, the time for 50% recrystallisation, and $t_c$, the time for complete recrystallisation) on initial grain-size is shown in Figure 60.

3.2.3.2. The effect of the matrix grain-size in two-phase alloys

The variation of hardness with time of annealing after 60% deformation is shown in Figure 61 for the Al - 1.10% Zr and Al - 6.97% Zr alloys with different initial grain-sizes. The pertinent data is presented in Table 7.

Figure 62 indicates the effect of initial grain-size on the recrystallisation times, $t_\frac{1}{2}$ and $t_c$, for these alloys.
3.2.3.3. The effect of the amount of prior deformation in two-phase alloys

The change in hardness as a function of the time of annealing after 30% and 60% deformation is shown in Figure 63 for all two-phase Al-Zr alloys. The data obtained from these curves is given in Table 7.

Figure 64 illustrates the effect of inter-particle spacing on the times of recrystallisation ($t_1^c$ and $t_2^c$).

The progress of recrystallisation during annealing at 335°C after 30% and 60% deformation is presented in Figure 65 for all two-phase alloys. Figure 66 indicates the variation of the parameter ($\frac{1}{1-x}$), where $x$ is the fraction recrystallised, as a function of the annealing time at 335°C. The data in this diagram fall on a series of straight lines. This indicates that recrystallisation occurred in accordance with the Avrami equation (equation (13)) (82). Table 8 gives values of $k$, (the constant in the Avrami equation), measured as the slope of the curves in Figure 66, for the various alloys.

The grain-size on completion of recrystallisation is shown as a function of inter-particle spacing in Figure 67.

Figure 68 illustrates the variation of the apparent nucleation and growth rates with inter-particle spacing.

Photomicrographs of the progress of recrystallisation of several two-phase Al-Zr alloys are presented in Figures 69-72.

3.2.4. Isothermal annealing at 375°C

The change in hardness as a function of time of annealing after 30% and 60% deformation is presented in Figure 73 for several Al-Zr alloys with similar initial grain-sizes. Table 9 collates the data obtained from these curves.

Figure 74 shows the relationship between the times of recrystallisation and inter-particle spacing.

The progress of recrystallisation during annealing at 375°C after 60% deformation is represented in Figure 75 for several Al-Zr alloys. Figure 76
illustrates the progress according to the Avrami equation (82). Table 10 gives the 'k' values obtained from Figure 76.

The grain-size on completion of recrystallisation is plotted as a function of inter-particle spacing in Figure 77.

Figure 78 illustrates the effect of inter-particle spacing on the apparent nucleation and growth rates.

A series of photomicrographs illustrates the progress of recrystallisation at 375°C after 30% and 60% deformation in Figures 79-84 for several Al-Zr alloys.

3.2.5. The effect of annealing temperature and time on two-phase alloys having similar initial grain-sizes

Figure 85 compares the isothermal annealing behaviour of several Al-Zr alloys at 335°C and 375°C after 60% deformation.

The relationship between the reciprocal of the annealing temperature and the time for 50% recrystallisation is shown in Figure 88 for several alloys after 60% deformation. The data for each alloy falls on a series of approximately parallel straight lines, which are of the form:

\[
\frac{1}{T} = a \log t_\frac{1}{2} + c \tag{37}
\]

where
- \(T\) = absolute temperature
- \(t_\frac{1}{2}\) = time for 50% recrystallisation
- \(a\) = constant in the range 0.5 to 0.7
- \(c\) = constant of the order of 0.0015
(a) Debye-Scherrer pattern of Al-1.10\%Zr powder.

(b) Debye-Scherrer pattern of Al-6.97\%Zr powder.

Fig. 40. X-ray identification of phases.
Table 3. Chemical analysis of alloys.

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<th>Alloy</th>
<th>B</th>
<th>L</th>
<th>N</th>
<th>M</th>
<th>D</th>
<th>A</th>
<th>Y</th>
<th>G</th>
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<td>3% Zr</td>
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Table 4. Dispersion parameters of two-phase Al-Zr alloys.

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<th>N_L</th>
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<th>D</th>
<th>C</th>
<th>H</th>
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<td>12.80</td>
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<td>-</td>
<td>0.61</td>
<td>0.07</td>
<td>51.97</td>
</tr>
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</table>
(a) Al-1.10% Zr; X 150.

(b) Al-2.36% Zr; X 150.

(c) Al-2.51% Zr; X 150.
(d) Al-3.43%Zr; X 150.

(e) Al-6.97%Zr; X 150.

(f) Al-9.18%Zr; X 150.
Fig. 41(a-i). The microstructure of the two-phase Al-Zr alloys.
(a) Al-1.10\%Zr; X 1300.

(b) Al-2.36\%Zr; X 2500.

(c) Al-3.43\%Zr; X 2200.
(d) Al-6.97%Zr; X 600.

(e) Al-9.18%Zr; X 700.

(f) Al-9.18%Zr; X 2700.
(g) Al-0.40%Zr; X 600.

(h) Al-0.34%Zr; X 600.

(i) Al-0.50%Zr; X 1200.
Fig. 42(a-1). The appearance of the second-phase particles in the various Al-Zr alloys.
Fig. 43(a-d). Effect of intermediate deformation on grain-size after annealing at 450°C for 48 hours. (SP Al and Al-0.02%Zr for 2 hours.)
(a) Al-1.10%Zr; X 104.

(b) Al-1.10%Zr; X 104.

(c) Al-2.36%Zr; X 104.
(d) Al-3.43\%Zr; X 104.

(e) Al-6.97\%Zr; X 104.

(f) Al-9.18\%Zr; X 104.
Fig. 44(a-i). Photomicrographs of the initial grain-sizes of several Al-Zr alloys.
(a) Al-2.36%Zr; 30% deformation; X 104.

(b) Al-2.36%Zr; 60% deformation; X 104.

(c) Al-6.97%Zr; 30% deformation; X 104.
Fig. 45(a-f). The cold-worked structures of several alloys.
Fig. 46(a-b). Effect of alloy content and initial grain-size on work-hardening behaviour.
Table 5. The amount of deformation required to produce an initial grain-size of 0.08mm after a 48 hour anneal at 450°C.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>$Zr$</th>
<th>DEFORMATION</th>
<th>PREDICTED GRAIN-SIZE</th>
<th>GRAIN-SIZE ACHIEVED</th>
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<td>48</td>
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<td>0.070</td>
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<tr>
<td>1.10</td>
<td>15</td>
<td>0.080</td>
<td>0.080</td>
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<td>0.070</td>
<td></td>
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<td>0.080</td>
<td>0.070</td>
<td></td>
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<tr>
<td>5.43</td>
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<td>0.069</td>
<td></td>
</tr>
<tr>
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<td>0.080</td>
<td>0.072</td>
<td></td>
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<td>0.080</td>
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<td>0.080</td>
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<td>45</td>
<td>0.080</td>
<td>0.058</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 47. Illustration of the "rate of change" technique used to determine $T_1$ and $T_2$ for SP Al and Al-0.02%Zr solid-solution $\frac{1}{2}$alloy C after 60% deformation.
(a) Initial grain-size of 0.565mm.

(b) Initial grain-size of 0.290mm.
(c) Initial grain-size of 0.263mm.

(d) Initial grain-size of 0.163mm.

Fig. 48(a-d). The effect of deformation and original grain-size on the isochronal annealing behaviour of a solid-solution alloy, Al-0.02%Zr.
Fig. 49(a-b). The effect of original grain-size on the isochronal annealing behaviour of Al-0.02%Zr alloy after (a) 30% and (b) 60% deformation.

Fig. 50. The recrystallised grain-size as a function of the initial grain-size for Al-0.02%Zr solid-solution.
(a) Al-0.02%Zr

(b) Al-1.10%Zr

(c) Al-1.30%Zr
Fig. 51(a-f). The effect of initial grain-size on the isochronal annealing behaviour of several Al-Zr alloys after 60% deformation.
Fig. 52(a-c). The effect of original grain-size on the recrystallisation temperatures of three alloys.
(a) Al-1.10%Zr

(b) Al-1.30%Zr
Fig. 53(a-d). The effect of initial grain-size on the fully recrystallised grain-size for various two-phase alloys.
Table 6. Isochronal annealing data.

(a) Al-1.10%Zr; initial grain-size of 0.070mm.
(b) Al-1.10%Zr; Initial grain-size of 0.225mm.

(c) Al-2.36%Zr; Initial grain-size of 0.070mm.

(d) Al-2.51%Zr; Initial grain-size of 0.073mm.
(e) Al-3.43%Zr; initial grain-size of 0.069mm; 60% deformation.

(f) Al-6.97%Zr; initial grain-size of 0.072mm.

(g) Al-9.18%Zr; initial grain-size of 0.074mm; 60% deformation.
(h) Al-0.34%Zr; initial grain-size of 0.133mm.

(i) Al-0.40%Zr; initial grain-size of 0.051mm.

(j) Al-0.54%Zr; initial grain-size of 0.038mm.

Fig. 54(a-j). The effect of deformation on the isochronal annealing behaviour of various Al-Zr alloys.
Fig. 55(a-c). Recrystallisation temperatures as a function of inter-particle spacing for 2-phase Al-Zr alloys.
Fig. 56. The fully recrystallised grain-size as a function of inter-particle spacing after 10, 30 & 60% deformation.

Fig. 57. The 50% recrystallisation temperature as a function of the final amount of deformation.

Fig. 58. The fully recrystallised grain-size as a function of the final amount of deformation.
(a) initial grain-size of 0.565mm.

(b) initial grain-size of 0.263mm.

(c) initial grain-size of 0.163mm.

Fig. 59(a-c). The effect of deformation and original grain-size on the isothermal annealing behaviour at 335°C of the solid-solution alloy, Al-0.02%Zr.
Fig. 60(a-b). The effect of initial grain-size and deformation on the isothermal annealing behaviour of the solid-solution alloy, Al-0.02%Zr.
Fig. 61(a-c). The effect of initial grain-size on the isothermal annealing behaviour at 335°C of three alloys after 60% deformation.
Fig. 62(a-c). The effect of initial grain-size and deformation on the isothermal annealing behaviour at 335°C of two two-phase alloys.
(a) Al-1.10%Zr; initial grain-size of 0.070mm.

(b) Al-1.10%Zr; initial grain-size of 0.225mm.

(c) Al-2.36%Zr; initial grain-size of 0.070mm.
(d) Al-2.51%Zr; initial grain-size of 0.073mm.

(e) Al-3.43%Zr; initial grain-size of 0.069mm; 60% deformation.

(f) Al-6.97%Zr; initial grain-size of 0.072mm.
(g) Al-6.97%Zr; initial grain-size of 0.100mm.

(h) Al-9.18%Zr; initial grain-size of 0.074mm; 60% deformation.

(i) Al-0.34%Zr; initial grain-size of 0.133mm.
(j) Al-0.40%Zr; initial grain-size of 0.051mm.

(k) Al-0.54%Zr; initial grain-size of 0.038mm.

Fig. 63(a-k). The effect of deformation on the isothermal annealing behaviour at 335°C of 2-phase Al-Zr alloys.

Table 7. Data from isothermal annealing at 335°C.
Fig. 64(a-b). The effect of inter-particle spacing and deformation on the isothermal annealing behaviour at 335°C of two-phase Al-Zr alloys.
Fig. 65(a-b). The progress of recrystallisation during isothermal annealing at 335°C.
Fig. 66. The progress of recrystallisation at 335°C after 60% deformation according to the Avrami equation.

Fig. 67. The fully recrystallised grain-size on annealing at 335°C after 60% deformation as a function of inter-particle spacing.
### Table 8

Table 8. *k* values for isothermal annealing at 335°C after 60% deformation for alloys with approximately similar initial grain-sizes.

<table>
<thead>
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<th>ALLOY % Zr</th>
<th>k</th>
</tr>
</thead>
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<tr>
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<td>1.4</td>
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<tr>
<td>1.10</td>
<td>0.7</td>
</tr>
<tr>
<td>2.36</td>
<td>0.5</td>
</tr>
<tr>
<td>3.43</td>
<td>0.5</td>
</tr>
<tr>
<td>6.97</td>
<td>0.4</td>
</tr>
<tr>
<td>9.18</td>
<td>0.5</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5</td>
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</table>

Fig. 68. Apparent nucleation and growth rates at 335°C as a function of inter-particle spacing, after 60% deformation.
Fig. 69 (a-c). The progress of recrystallisation during isothermal annealing at 335°C after 30% deformation for an Al-2.36%Zr alloy.
Fig. 70(a-c). The progress of recrystallisation during isothermal annealing at 335°C after 60% deformation for an Al-1.10%Zr alloy with an initial grain-size of 0.225mm.
Fig. 71(a-c). The progress of recrystallization during isothermal annealing at 335°C after 60% deformation for an Al-6.97%Zr alloy with an initial grain-size of 0.070mm.
Fig. 72(a-c). The progress of recrystallization during isothermal annealing at 335°C after 60% deformation for an Al-0.50%Zr alloy.
(a) Al-0.02%Zr; initial grain-size of 0.163mm; 60% deformation.

(b) Al-1.10%Zr; initial grain-size of 0.070mm.

(c) Al-6.97%Zr; initial grain-size of 0.072mm.
(d) Al-0.34%Zr; initial grain-size of 0.133mm; 60% deformation.

(e) Al-0.40%Zr; initial grain-size of 0.051mm; 60% deformation.

(f) Al-0.54%Zr; initial grain-size of 0.038mm; 60% deformation.

Fig. 73(a-f) The isothermal annealing behaviour at 375°C of various Al-Zr alloys.
(a) after 30% deformation.

(b) after 60% deformation.

Fig. 74(a-b). The effect of inter-particle spacing and deformation on the times of recrystallisation at 375°C.
Fig. 75. The progress of recrystallisation at 375°C after 60% deformation.

Fig. 76. The progress of recrystallisation during isothermal annealing at 375°C after 60% deformation according to the Avrami equation.
<table>
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<th>INITIAL CHAIN SIZE</th>
<th>% DIFFUSION</th>
<th>$t_1$ mins</th>
<th>$t_2$ mins</th>
<th>$t_1$ - $t_2$ mins</th>
<th>ALL-HYPERCRITICIZED CHAIN SIZE</th>
<th>$k'/m^2/sec$</th>
<th>$e'$ m/sec</th>
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Table 9. Data from isothermal annealing at 375°C.

<table>
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<th>ALLOY % Zr</th>
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<tbody>
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<tr>
<td>1.10</td>
<td>1.1</td>
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<td>2.1</td>
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<tr>
<td>0.34</td>
<td>1.7</td>
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<tr>
<td>0.50</td>
<td>2.1</td>
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Table 10. $k$ values for isothermal annealing at 375°C after 60% deformation.
Fig. 77. The fully recrystallised grain-size on annealing at 375°C after 60% deformation as a function of interparticle spacing.

Fig. 78. Apparent nucleation and growth rates on annealing at 375°C after 60% deformation as a function of interparticle spacing.
Fig. 79(a-b). The progress of recrystallisation during isothermal annealing at 375°C after 30% deformation for an Al-1.10%Zr alloy with an initial grain-size of 0.070mm.
Fig. 8.0(a-c). The progress of recrystallisation during isothermal annealing at 375°C after 30% deformation for an Al-6.97%Zr alloy with an initial grain-size of 0.072mm.
Fig. 81(a-c). The progress of recrystallisation during isothermal annealing at 375 °C after 60% deformation for an Al-1.10%Zr alloy with an initial grain-size of 0.070 mm.
Fig. 82(a-b). The progress of recrystallization during isothermal annealing at 375 °C after 60% deformation for an Al-6.97%Zr alloy with an initial grain-size of 0.072 mm.
Fig. 83(a-b). The progress of recrystallisation during isothermal annealing at 375°C after 60% deformation for an Al-0.50%Zr alloy.

Fig. 84. Microstructure of an Al-0.40%Zr alloy after isothermal annealing at 375°C for 1000 minutes after 60% deformation.
(a) Al-0.02%Zr; initial grain-size of 0.163mm.

(b) Al-1.10%Zr; initial grain-size of 0.070mm.

(c) Al-6.97%Zr; initial grain-size of 0.072mm.
(d) Al-0.34%Zr; initial grain-size of 0.133mm.

(e) Al-0.40%Zr; initial grain-size of 0.051mm.

(f) Al-0.54%Zr; initial grain-size of 0.038mm.

Fig. 85(a-f). Comparison of the isothermal annealing behaviour at 335°C & 375°C after 60% deformation.
Fig. 86. Relationship between the reciprocal of the absolute temperature and the time for 50% recrystallisation for several Al-Zr alloys.

Table 11. Comparison of the values of inter-particle spacing from different formulae for a range of dispersion data. (For spherical particles; radii and spacings in microns.)
4. DISCUSSION

4.1. Present results

4.1.1. Comparison of the formulae available for the evaluation of inter-particle spacing in two-phase alloys.

It is clear from the published literature (see section 1.4.7.) that the rate of recrystallisation can be accelerated or retarded by the presence of second-phase particles, the governing factors being the size and spacing of the particles. However, it has proved difficult to evaluate the results of previous investigations on account of the variety of formulae for inter-particle spacing that has been used and the failure to present sufficient relevant data. In other studies, quantitative results have been presented, but have been interpreted by means of formulae which are either not applicable to the dispersion microstructures reported or which are open to certain basic criticisms.

A comprehensive survey of the various definitions and formulae which have been used to describe the inter-particle spacing has, therefore, been undertaken, in conjunction with a parallel investigation of the recrystallisation of iron-alumina dispersion alloys. (See appendix). This has shown that the differences between the formulae, which arise from the various definitions and assumptions, lead to characteristically different values of the inter-particle spacing for any given microstructure. Table 11 indicates the variation in results from the various formulae for a range of hypothetical alloys containing spherical particles.

In order to choose a suitable inter-particle spacing formula for the assessment of recrystallisation, the following points were considered relevant. Firstly, the formation of a nucleus is a three-dimensional process and the controlling factor in two-phase alloys is probably the distance between any particle and its nearest neighbour in any direction. Such a distance determines the volume of the matrix in which a nucleus can form. Secondly, nucleation often involves the re-arrangement of a dislocation sub-structure, the walls of which frequently pass through second-phase particles. Thirdly, the formula must be selected on the basis of particle distributions that are
consistent with the observed microstructures. Random distributions are normally observed, and, hence, it is necessary to avoid errors introduced by wrongful assumption of a uniform dispersion.

The supplementary survey, therefore, concluded that the interpretation of recrystallisation data should be based on inter-particle spacing values which are calculated as the centre-to-centre nearest neighbour distance in the volume i.e. \( \Delta_3 \) as given by equation (32). In order to calculate \( \Delta_3 \), the number per unit volume and the shape of the second-phase particles need to be known.

In the present investigation, the particles have been approximated to the ideal shape of a square plate. This has been justified by the good agreement between the calculated and measured dimensions. (See Table 4).

4.1.2. The annealing of solid-solution alloys

The main objective of the investigation was to study the effect of second-phase particles on recrystallisation behaviour. Hence, the study of solid-solution alloys was restricted to a comparison of the behaviour of an Al - 0.02 % Zr alloy with that of super-pure aluminium. Figure 47 illustrates the effect of adding 0.02 wt. % Zr in solid-solution to super-purity aluminium. Both the temperatures for 50% recrystallisation and complete recrystallisation are raised. This is consistent with more thorough work (107, 110, 114) which reported that increasing the solute content in solid-solution leads to a decrease in high-angle boundary mobility. (See section 1.4.6.).

The effects of deformation and original grain-size on the annealing behaviour of the Al - 0.02 % Zr solid-solution are shown in Figures 48 and 49. An increase in original grain-size raises \( T_c \) (the temperature at which recrystallisation is completed) and \( T_{1/2} \) (50% recrystallisation temperature), with \( T_c \) increasing more than \( T_{1/2} \) after both 30 and 60% deformation. This effect is greater the lower is the amount of prior deformation. Figure 50 indicates that the grain-size after primary recrystallisation decreases as the original grain-size decreases and the amount of prior deformation increases.

These observations are consistent with all previous work. Increasing the amount of prior deformation causes an increase in the retained stored energy
of cold work. This induces a reduction in the recrystallisation temperatures. The finer the initial grain-size, the greater the number of possible nucleation sites, and the finer is the fully recrystallised grain-size. The effect of original grain-size becomes less pronounced as the final amount of deformation is increased.

The effect of initial grain-size on the apparent nucleation and growth rates of the solid-solution alloy is summarised in Table 7, which confirms that decreasing the grain-size causes an increase in the nucleation rate, but has less effect on the apparent growth rate.

4.1.3. The isochronal annealing of two-phase alloys

In order to determine the true effect of particle concentration on recrystallisation, any other factor which may influence recrystallisation behaviour must be kept constant.

One factor which can affect the recrystallisation temperatures of two-phase alloys is the composition of the matrix solid-solution. This has been controlled by annealing at 450°C for 48 hours, followed by quenching in order to retain the Zr content at 450°C in solid-solution to room temperature.

The final amount of deformation is a further factor which influences annealing behaviour. By ensuring that each alloy has the same amount of reduction in thickness (10, 30 or 60%), direct comparisons can be made.

The original grain-size (i.e. the grain-size immediately prior to the final deformation) is another variable which can affect the process of recrystallisation. This effect was established for three two-phase Al-Zr alloys after 60% deformation. For further studies, the effect was eliminated by ensuring that each alloy had the same initial grain-size.

4.1.3.1. The effect of matrix grain-size.

The effect of varying the initial grain-size on recrystallisation has been determined for alloys containing 1.10% Zr, 1.30% Zr and 9.18% Zr. Different starting grain-sizes were achieved by varying the amount of deformation carried out during the solid-solution standardisation treatment. The effect of this treatment is shown in Figure 43 (a-b).
Each alloy with a spread of initial grain-sizes was finally deformed by 60% and isochronally annealed for one hour. The recrystallisation temperatures and fully recrystallised grain-sizes were determined. Figure 52 (a-c) indicates the dependence of the recrystallisation temperatures on initial grain-size. The behaviour of an alloy containing 1.10 or 1.30 % Zr is more sensitive to changes in original grain-size than the Al - 9.18% Zr alloy. That is, increasing the number and size of Al\textsubscript{3}Zr particles leads to a decreasing sensitivity of the recrystallisation temperatures to variations in the original grain-size.

The temperature for the completion of recrystallisation is most affected and the temperature for the onset of recrystallisation the least affected by changes in the initial grain-size. For the Al - 1.10 and - 1.30 % Zr alloys, the temperature range required to complete the recrystallisation process is increased as the original grain-size increases. For the Al - 9.18% Zr alloy, hardly any effect is discernible.

Figure 53 (a, b, d) shows the relationship between original grain-size and the final, fully recrystallised grain-size. The degree of grain-refinement is greater for large initial grain-sizes. For fine original grain-sizes, it is of the order of 2:1; and for large grain-sizes, it is 6:1, and is independent of the alloy composition. Grain refinement is probably a function of the total amount of deformation given to the alloys. The fully recrystallised grain-size decreases for a constant initial grain-size as the number of second-phase particles increases. This implies the increased nucleation of recrystallised grains at particles.

4.1.3.2. The effect of prior deformation

Figure 54 shows the effect of final deformation on the isochronal annealing behaviour of all two-phase alloys. Those alloys containing coarse particles ($L_3 > 2$ microns) produced by the forging of as-cast structures were given final deformations of 10, 30 and 60%. Alloys with fine particles ($L_3 < 1$ micron) produced by precipitation from super-saturated solid-solutions had final reductions in thickness of 30 and 60%.

Figure 46 indicates that increasing the final amount of deformation causes
an increase in the hardness of all the alloys. Also, the greater the number of particles, the harder the alloy becomes after deformation. Since there is no noticeable difference between the rates of hardness increase for the various alloys, it can be concluded that there is no significant variation of their work-hardening behaviour as the particle content increases.

The effect of final deformation on the recrystallisation temperatures of two-phase Al-Zr alloys can be determined from Figure 55. For all alloys, increasing the amount of deformation causes a decrease in all the recrystallisation temperatures. The recrystallisation temperature range decreases only slightly as the amount of deformation increases.

Figure 57 shows the effect of deformation on the temperature for 50% recrystallisation for three alloys containing coarse particles. Increasing the amount of deformation and/or increasing the number of particles causes a decrease in the 50% recrystallisation temperature. This temperature increases rapidly below a reduction in thickness of about 20%. The fully recrystallised grain-size is shown as a function of the final amount of deformation in Figure 58 for the same three alloys. Increasing the amount of deformation and/or increasing the number of particles produces a finer recrystallised grain-size.

The effect of increasing the number of coarse particles can be interpreted in terms of the increased nucleation of recrystallised grains. (See section 4.1.4.3.). At deformation below about 20%, the fully recrystallised grain-size is larger than the original grain-size, presumably because the critical amount of deformation is being approached. Nevertheless, increasing the number of coarse particles still causes a finer recrystallised grain-size to be produced.

The significance of the final amount of deformation on recrystallisation can be summarised as follows. The larger the deformation, the lower are the recrystallisation temperatures, the narrower the recrystallisation temperature range and the finer the as-recrystallised grain-size. These observations can be explained in terms of the increase in strain-energy stored in the alloys as the amount of deformation is increased. Originally, it was intended to study thin films of the cold-worked structures to enable an interpretation to be made in terms of the formation, size and growth of sub-grains. Unfortunately, owing
to the particle size in the alloys, successful thin films could not be obtained. However, it has been pointed out that coarse particles aid the formation of sub-grains in the cold-worked structure (15). The greater the amount of deformation, the smaller will be the size of a growing sub-grain when it acquires a high-angle boundary. Therefore, a lower temperature for a given time is necessary for the growing sub-grain to become an active nucleus, and the resultant grain-size is finer.

4.1.3.3. The effect of particle size and concentration

In order to determine the effect of second-phase $\text{Al}_3\text{Zr}$ particles on the recrystallisation behaviour of super-pure aluminium, the other variables which can affect such behaviour first had to be eliminated.

The solid-solution content of the matrix was standardised as mentioned earlier (Section 2.2.4.). The effect of initial grain-size was eliminated by aiming at a constant value. This was accomplished by applying a predetermined amount of deformation prior to the standardisation of solid-solution treatment. Table 5 indicates the amount of deformation applied to each alloy to furnish a grain-size of about 0.08 mm. Good reproduction of grain-sizes was obtained for those alloys containing coarse particles. However, this was not the case for alloys with fine particles. This is not considered too important as earlier investigations (Section 4.1.4.1.) indicate that any grain-size effect diminishes as the concentration of second-phase particles is increased to such an extent that, in the finer dispersion, there is virtually no variation in recrystallisation behaviour with grain-size.

After standardisation of both the solid-solution content and the initial grain-size, each alloy was finally deformed by 10, 30 and 60% reductions in thickness and isochronally annealed. Figure 54 shows the change in hardness with annealing temperature for each deformation. Recrystallisation temperatures have been plotted as a function of the inter-particle spacing, $\Delta_3$ (or $\Delta_3 - L_3$) in Figure 55. This spacing is a direct function of the particle concentration by definition. $\Delta_3 - L_3$ has been used on a few diagram (e.g. Figures 55 and 56) in an attempt to minimise the effect of the different particle sizes. $\Delta_3$ is the centre-to-centre nearest neighbour distance, and it is suggested that $\Delta_3 - L_3$ represents the effective mean edge-to-edge nearest neighbour spacing.
Figures 55 (a) and 64 (a) show that plots against $\Delta_3 - L_3$ are always parallel to those against $\Delta_3$. This appears not to be the case in all the other diagrams, merely due to the use of a logarithmic scale.

It is convenient to describe the effects determined in two stages: those for alloys having widely spaced, coarse particles ($\Delta_3 > 7$ microns; $L_3 > 2$ microns); and those for alloys containing fine, closely spaced second-phase particles ($\Delta_3 < 3$ microns; $L_3 < 1$ micron).

Figure 55 indicates that increasing the number of coarse particles causes a decrease in the recrystallisation temperatures and the recrystallisation temperature range. The temperature for the completion of recrystallisation is most affected, the temperature for the start of recrystallisation the least. Figure 56 shows that, as the number of coarse particles is increased, the fully recrystallised grain-size is reduced. Thus, the presence of coarse, widely spaced particles enhances the recrystallisation process with the production of a fine grain-size. For every alloy, the temperature for 50% softening, $S_{1/2}$, is lower than the temperature for 50% recrystallisation, $T_{1/2}$, indicating the extent of softening due to recovery.

The composition of the solid-solution in equilibrium at 450°C has been determined as 0.03% Zr, by extrapolating the results of Fink and Willey (152). The solid-solution alloy, Al - 0.02% Zr, has the composition nearest to this, and it has a 50% recrystallisation temperature of 310°C. This figure has been arrived at by extrapolating Figure 49 (b) to an initial grain-size of 0.070 mm. It is at least 60°C higher than the equivalent temperature for super-pure aluminium.

In the case of the two-phase alloys, the recrystallisation temperature range is greatest for the alloy with the widest spacing (Al - 1.10% Zr), and this alloy has a 50% recrystallisation temperature of 332°C. This alloy has the nearest two-phase composition to the theoretical limit of solid-solubility (0.03% Zr). Also, an Al - 0.5% Zr solid-solution alloy has a reported 50% softening temperature of 440°C (141). It, therefore, seems reasonable to suppose that increasing the solid-solution content from 0.02 to 0.03% Zr would raise the 50% recrystallisation temperature from 310°C to the order of 335°C. This would then be in accordance with the findings of Mould and Cotterill (124) for Al-Fe solid-solutions. They reported that the recrystallisation
temperature range is greatest for the solid-solution content having the largest equilibrium solute content and for the dispersion alloy having the smallest concentration of second-phase particles.

In order to determine whether the trend of decreasing recrystallisation temperatures would continue for greater numbers of second-phase particles, attempts were made to produce alloys with a zirconium content higher than 7%. However, such alloys proved impossible to forge due to the brittleness of the $\text{Al}_3\text{Zr}$ network in the resultant as-cast structures. Higher particle concentrations were, therefore, achieved by precipitation from super-saturated solid-solutions. Similarly shaped particles were obtained but they were much finer in size ($L_3 < 1 \ \mu m$).

Figure 55 (b, c) indicates that increasing the concentration of fine particles (i.e., decreasing $\Delta_3$ below 3 $\mu m$) causes an increase in the recrystallisation temperatures and the recrystallisation range. The temperature at which recrystallisation ends increases at a greater rate than the 50% recrystallisation temperature. There is a slight suggestion that the temperature at which recrystallisation begins may increase as the particle concentration increases. Figure 56 indicates that increasing the number of fine particles induces an increase in the fully recrystallised grain-size until, eventually, it is larger than the original grain-size. Thus, the presence of fine, closely spaced second-phase particles inhibits the recrystallisation process, with the production of a coarse grain-size.

Therefore, the introduction of second-phase $\text{Al}_3\text{Zr}$ particles can have opposing effects on the recrystallisation behaviour of super-pure aluminium. For coarse, widely spaced particles, the recrystallisation process is enhanced whereas for closely spaced, fine particles, the opposite is the case. Between the two situations, a minimum recrystallisation temperature range must exist at some intermediate inter-particle spacing (and particle size?). Such a critical inter-particle spacing has been suggested (124) and Doherty and Martin (122) have reported a change-over in the influence of fine dispersions of Cu $\text{Al}_2$ on the recrystallisation behaviour of aluminium.

Figure 55 emphasises the importance of examining the whole recrystallisation temperature range to verify the effect of controlled variables on the recrystallisation process.
4.1.4. Recrystallisation kinetics in two-phase alloys

4.1.4.1. The effect of grain-size

Figures 59 and 61 show the hardness-annealing time curves for the solid-solution alloy, Al - 0.02 % Zr, and the dispersion alloys, Al - 1.10 % Zr and Al - 6.97 % Zr, after two final deformations. Figures 60 and 62 show the relationship between the times of recrystallisation (i.e. $t_c$, the time for completion of the process; and $t_{1/2}$, the time for 50% recrystallisation) and the initial grain-size. It can be seen that, as the original grain-size is reduced, the recrystallisation times decrease. The time for completion of the process decreases at a greater rate than the time for 50% recrystallisation. These effects are more pronounced in the solid-solution alloy and the Al - 1.10 % Zr alloy than in the Al - 6.97 % Zr alloy with a higher concentration of particles. Such observations are consistent with the effect of original grain-size on isochronal annealing behaviour.

4.1.4.2. The effect of prior deformation

A comparison of Figures 54 to 58 and Table 6 with Figures 63 to 67 and Table 7 shows that the results of isothermal annealing are consistent with those determined during isochronal annealing (Section 3.2.2.3.). For all alloys, increasing the amount of final deformation greatly enhances the recrystallisation process i.e. the times of recrystallisation are reduced and the as-recrystallised grain-size is finer. However, for those alloys containing the fine, closely spaced particles, 30% reduction in thickness does not induce subsequent recrystallisation.

4.1.4.3. The effect of particle concentration

Figure 63 shows the 'change' in hardness with time of annealing at 335°C for several two-phase alloys with similar initial grain-sizes. The results of metallographic determinations of the extent of recrystallisation with annealing time are presented in Figure 65. All the alloys which recrystallise show typical "S"-shaped curves. The times for 50% recrystallisation and complete recrystallisation are plotted as functions of inter-particle spacing in Figure 64. Table 7 gives the exact values of $t_{1/2}$ and $t_c$, the variations in
which indicate a large difference in recrystallisation kinetics.

Increasing the concentration of coarse particles causes a reduction in the times of recrystallisation, the time for completion being more affected than the time for 50% recrystallisation. This is in complete agreement with the findings for isochronal annealing (section 3.2.2.), and provides direct evidence that alloys with a larger concentration of coarse particles produce higher recrystallisation rates. The shortening of the isochronal recrystallisation temperature range as the number of coarse particles increases is, therefore, an indication of an increasing recrystallisation rate. This clearly suggests that coarse particles enhance the recrystallisation process.

For alloys with fine particles, only the one with the least number of particles fully recrystallises, and then only at the higher deformation (Al - 0.5% Zr). The addition of more particles completely suppresses recrystallisation after both 30% and 60% reductions in thickness. This is also in complete agreement with the isochronal annealing behaviour of these alloys. (Section 3.2.2.).

In Figure 66, the progress of isothermal recrystallisation is presented according to the Avrami equation (82). (See equation (13) in section 1.4.4.). Plots of $\ln \left( \frac{1}{1 - x} \right)$ against $t$ (where $x =$ the fraction recrystallised; and $t =$ the time of annealing) give a straight line with a gradient of $K$. Values of $K$, the constant in the Avrami equation, are listed in Table 8. For all two-phase alloys, $K$ values are of the order of 0.6. Cahn (6) has reported the measurement of $K$ values in the range 1 to 2, the exact figure varying with the experimental conditions and alloy content. A low value of $K$ implies one or two dimensional recrystallisation. That is, new recrystallised grains grow in the form of rods or platelets. Extensive metallographic examinations of the specimens indicated that this was clearly not the case in the present investigation, but that the shape of the newly-formed recrystallised grains was always consistent with three-dimensional behaviour. Ryum (141) reported a $k$ value of about 1 for an Al - 0.5% Zr alloy. A similar value was obtained by Sundberg et al. (143) in their investigation. Therefore, this kind of analysis of the kinetics of isothermal recrystallisation does not yield meaningful results.
The effect of increasing the concentration of coarse particles on isothermal annealing behaviour is illustrated in Figure 67 and is to cause a reduction in the fully recrystallised grain-size. This is further evidence that coarse particles enhance nucleation and cause an acceleration of the entire recrystallisation process. This has also been demonstrated by, among others, Leslie et al. (108) for two-phase Fe-O alloys, Blade (123) and Mould and Cotterill (124) for two-phase Al-Fe alloys, and Doherty and Martin (122) for two-phase Al-Cu alloys. Metallographic evidence for the nucleation of grains at coarse particles is provided in Figures 69, 71, 79, 80, 81. (The effect is clearer for alloys deformed 30%). It can also be seen that the as-recrystallised structure becomes finer and more uniform as the number of coarse particles increases.

The apparent nucleation and growth rates are shown as functions of inter-particle spacing in Figure 68. The nucleation rate varies to a greater extent than the growth rate, confirming the importance of nucleation at coarse particles for accelerated recrystallisation. The nucleation rate increases slowly at wide spacings but rises at an increasing rate as the spacing is reduced. The diagram also indicates that the alloy containing very coarse particles (Al - 9.18% Zr) has a much higher nucleation rate (closed square symbol) than an alloy having less coarse particles similarly placed (e.g. alloy Al - 1.10% Zr, closed round symbol).

On the other hand, increasing the concentration of fine particles has suppressed the recrystallisation process completely. Doherty and Martin (122) have provided evidence that nucleation becomes difficult at very small spacings between fine particles.

It is, therefore, clear that the recrystallisation process is enhanced both isothermally and isochronally by an increase in the concentration of coarse particles, the acceleration being associated with an increase in nucleation rate. As the number of fine particles increases, the process is retarded. An annealing temperature of 335°C was not high enough to determine any apparent nucleation and growth rates for these alloys.

4.1.4.4. The effect of annealing temperature

Further isothermal annealing experiments were carried out at 375°C so
that a comparison of nucleation and growth rates could be made between alloys with coarse particles and those containing fine particles. Figure 73 shows the change in hardness as a function of annealing time. The progress of recrystallisation is illustrated in Figure 75, and Figure 76 represents the extent of recrystallisation according to the Avrami equation (82) (equation (13)). The trends are the same as those outlined in section 4.1.4.3. for isothermal annealing at 335°C apart from the fact that, at 375°C, only the alloy with the greatest number of fine particles (Al - 0.40 % Zr) does not recrystallise.

The as-recrystallised grain-size is shown as a function of inter-particle spacing in Figure 77. Alloys with coarse particles behave as described previously (section 4.1.4.3.). For alloys with fine particles, increasing the particle concentration results in an increase in the as-recrystallised grain-size until it is eventually coarser than the original grain-size. Figure 84 indicates the lack of recrystallisation at 375°C after 60% deformation in the Al - 0.40 % Zr alloy having a $\Delta_3$ value of 1.75 microns.

The effect of temperature on the isothermal annealing behaviour is illustrated in Figure 85. It is obvious that an increase in temperature causes a reduction in the times for complete recrystallisation. There is no significant difference in the fully recrystallised grain-sizes obtained after annealing at different temperatures. Figure 86 summarises the relationship between the temperature of annealing and the time for 50% recrystallisation.

Apparent nucleation and growth rates have been calculated for the alloys at 375°C, and Figure 78 expresses them as a function of inter-particle spacing. It can again be seen that the nucleation rate shows the greater sensitivity to changes in the concentration of second-phase particles. Decreasing the $\Delta_3$ spacing between fine particles below 3 microns causes a decrease in both nucleation and growth rates. The nucleation rate is reduced more drastically than the growth rate. Alloys containing coarse particles behave as outlined in section 4.1.4.3. This is further evidence that it is the nucleation of recrystallised grains (or lack of it) at particles which causes the recrystallisation process to be enhanced (or retarded).

Therefore, the recrystallisation process is accelerated or retarded both isochronally and isothermally, depending upon the size and concentration of second-phase particles. For widely spaced, coarse particles ($\Delta_3 > 7 \ \mu m; L_3 > 2 \ \mu m$), recrystallisation is enhanced and fine resultant grain-size is
obtained. For fine, closely spaced particles (\( \Delta_3 < 3 \mu m; L_3 < 1 \mu m \)),
the process is retarded with the production of a coarse grain-size.
4.2. The mechanism of recrystallisation in two-phase alloys

The experimental observations concerning the annealing behaviour of Al-Zr alloys containing second-phase \( \text{Al}_3\text{Zr} \) particles clearly show that the progress of recrystallisation is nucleation dependent. Therefore, the effect of second-phase particles on recrystallisation must be interpreted in terms of changes in the nucleation rate.

4.2.1. The Mould-Cotterill hypothesis

Swann (15) has shown that the interactions between coarse particles and dislocations, which occur during the deformation of two-phase alloys, aid the development of a sub-grain structure. Fine particles (\(< 1\) micron diameter), however, inhibit the formation of a cell structure during deformation. (Section 1.2.4.3.). The nucleation mechanism proposed by Hu (68) suggests that the neighbouring sub-grains which were formed during deformation coalesce to form recrystallisation nuclei with high-angle boundaries (Section 1.4.2.3.).

Mould and Cotterill (124) have proposed a model for the recrystallisation of two-phase alloys on the basis of Hu's nucleation mechanism. They combined their own results for aluminium-iron alloys with Doherty and Martin's data (122) for aluminium-copper alloys to postulate the effect of changes in the inter-particle spacing on the formation and growth of recrystallised grains from within a deformation sub-structure.

According to this hypothesis, for solid-solution alloys, nucleation occurs in the vicinity of the original grain-boundaries or in regions of high lattice curvature formed inside the grains during the deformation process. The addition of a small number of particles provides more nucleation sites with a resultant acceleration of the recrystallisation process. The particles cause local concentrations of the distortion produced during deformation, and it is, in fact, the interfaces of the particles with the surrounding matrix which act as sites for nucleation. Any increase in the particle concentration leads to further increases in the nucleation rate as long as there is sufficient space between particles to permit the nucleation of new grains.

Eventually, an inter-particle spacing, \( \Delta_A \), is reached when recrystallisation
nuclei can no longer be produced at each particle due to the impingement of embryos before they reach a viable size. Hence, the nucleation rate is decreased. Further decreases in the inter-particle spacing produce further reductions in the nucleation rate until the nucleation of grains at particle/matrix interfaces is completely suppressed. This occurs at an inter-particle spacing, $\Delta_A$, of the order of the diameter of the deformation sub-grains when the sub-grain walls are pinned by particles. This prevents the coalescence of sub-grains into viable nuclei. Further drastic reductions in the nucleation rate occur as nucleation can now only take place at the original grain-boundaries by a mechanism of the type proposed by Beck and Sperry (77). (Section 1.4.2.5.).

The growth of recrystallised grains occurs by the movement of high-angle boundaries through the surrounding matrix. For alloys with inter-particle spacing values greater than $\Delta_A$, the boundaries of all the nuclei impinge on each other before reaching other particles. There will, therefore, be no significant change in the growth rate between $\Delta_C$ and $\Delta_A$. At spacings less than $\Delta_A$, mobile boundaries have to circumnavigate those particles that have not produced a viable nucleus before meeting other boundaries. The growth rate is, therefore, reduced. At spacings below $\Delta_B$, the growth rate is reduced even further as nuclei only form at the original grain-boundaries, and any mobile boundary has to overcome the restraint imposed by a large number of particles before impingement with other boundaries.

By correlating the kinetics of recrystallisation and the inter-particle spacing (see Figure 34) for Al-Fe and Al-Cu alloys, Mould and Cotterill (124) obtained the following values for the critical spacings:

$$\Delta_A = 4 \text{ microns and } \Delta_B = 1.8 \text{ microns}.$$

4.2.2. The present investigation

The values for the critical spacings obtained by Mould and Cotterill (124) are larger than expected on the basis of the minimum size of a viable nucleus and the deformation cell size for their alloys. They were obtained by means of an analysis due to Shaw et al. (167), who gave the volumetric mean free path as:
and the nearest neighbour distance in a volume as:

\[ \frac{R}{1 - \sqrt{\frac{1}{2} \left( \frac{r}{R} \right)^2}} - r \]

...(38)

and the nearest neighbour distance in a volume as:

\[ 2r \left( \frac{1}{F_R} \right)^{\frac{1}{3}} \]

...(39)

where  

- \( R = \) the radius of a spherical domain containing a particle and its associated solid-solution  
- \( r = \) the particle radius  
- \( F_R = \) the volume ratio

It has been pointed out (see appendix), however, that use of the equations derived by Shaw et al. (167) yields dubious values for the various parameters. Therefore, the values for inter-particle spacing have been re-calculated from the data for Al-Fe (124) and Al-Cu (122) alloys in terms of \( \Delta_3 \) (equation (32)), the centre-to-centre nearest neighbour distance in a volume for randomly dispersed particles. They are presented in Tables 12 and 13.

Tables 12 and 13 also show the values for the apparent nucleation and growth rates for the two alloy systems which have been re-calculated to yield the same units. Figure 87, therefore, presents the revised variation of the apparent nucleation and growth rates with \( \Delta_3 \). The new critical spacing values obtained from Figure 87 are: \( \Delta_A \) (the spacing at which the forming embryos interfere with each other before reaching a viable size) is 2 microns; and \( \Delta_B \) (of the order of the deformation sub-grain size) is 0.8 microns. Neither of the investigations (122, 124) have reported the dislocation sub-structures involved. However, the theoretical values of \( \Delta_A \) and \( \Delta_B \) can be postulated by making use of the knowledge that the sub-grain size in heavily deformed aluminium is normally of the order of 1 to 2 microns. Therefore, according to the Mould-Cotterill hypothesis, \( \Delta_A \) will be of the order of twice the sub-grain diameter i.e. \( \Delta_A = 2 \) to 4 microns. The nucleation of recrystallised grains at each particle will be completely prevented when the inter-particle spacing is equal to or less than the sub-grain diameter i.e \( \Delta_B = 1 \) to 2 microns. There is, therefore, good agreement between the predicted and experimentally determined values for the critical spacings.
Table 12. Re-calculation of Doherty and Martin's results (122) for the isothermal annealing of two-phase Al-Cu alloys at 305°C after 60% deformation.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>ε</th>
<th>N</th>
<th>Δ</th>
<th>m'</th>
<th>G'</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>X10^-2</td>
<td>X10^10/ce</td>
<td>micron</td>
<td>m^2/sec</td>
</tr>
<tr>
<td>3C</td>
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<td>21</td>
<td>0.44</td>
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<tr>
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<td>1.90</td>
<td>5.6 x10^-3</td>
<td>1.4 x10^-4</td>
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<tr>
<td>7D</td>
<td>6D</td>
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<td>9.8 x10^-6</td>
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<tr>
<td>10D</td>
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<td>110</td>
<td>0.54</td>
<td>2.0 x10^-4</td>
<td>2.5 x10^-5</td>
</tr>
<tr>
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<td>1.4 x10^-4</td>
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</tr>
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</table>

Table 13. Re-calculation of Mould and Cotterill's results (124) for the isothermal annealing of two-phase Al-Fe alloys at 300°C after 60% deformation.

<table>
<thead>
<tr>
<th>ALLOY</th>
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<th>Δ</th>
<th>m'</th>
<th>G'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>X10^-2</td>
<td>X10^10/ce</td>
<td>micron</td>
<td>m^2/sec</td>
</tr>
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<td>0.34</td>
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<td>1.85</td>
<td>2.08</td>
<td>0.67</td>
<td>2.94 x10^-5</td>
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Fig. 87. Apparent nucleation and growth rates as functions of inter-particle spacing for Al-Cu and Al-Fe alloys annealed at 300-305°C after 60% deformation.

Fig. 88. Fully recrystallised grain-size on annealing at 305°C after 60% deformation as a function of inter-particle spacing for Al-Cu alloys. (From the data presented by Doherty and Martin (122).)
The fact that the two sets of curves in Figure 87 do not meet is probably a function of the different effects that copper and iron in solid-solution have on the recrystallisation of aluminium.

The present experimental results and observations can be rationalised in terms of the Mould-Cotterill hypothesis.

Figure 46 indicates that there is no significant change in work-hardening behaviour due to the presence of second-phase particles. There will, therefore, be no additional stored energy of cold-work due to the particles. However, there will probably be local differences in the degree of work-hardening between matrix regions adjacent to particles and particle-free areas. As the increased amount of distortion at particle/matrix interfaces accounts for the increased nucleation, the influence of the final amount of deformation can be explained.

The larger the deformation, the smaller will be the size of a growing sub-grain when it acquires a high-angle boundary. Therefore, a shorter time at a given temperature (or a lower temperature for a given time) is necessary before an active nucleus is formed. Increasing the number of coarse particles aids the development of a sub-grain structure during deformation (15). Therefore, an increase in the particle concentration, and/or the amount of prior deformation, can be expected to reduce the time or temperature for the completion of recrystallisation and to lead to a finer recrystallised grain-size. (See Tables 6, 7 and 9). At low deformations, (similar to but greater than the critical amount of deformation), increasing the particle concentration still produces an increasing nucleation rate with the result of finer recrystallised grain-sizes.

For particle-retarded recrystallisation, only the higher amounts of deformation will encourage the formation of new grains as the presence of fine particles either prevents sub-grain formation or pins the sub-grain walls (e.g. Figures 54 (i) and 63 (k)).

In particle-accelerated recrystallisation, the larger the particle size, the greater will be the particle/matrix interface and, therefore, the amount of inhomogeneous deformation in these regions will be greater. The rate of nucleation of recrystallised grain will be higher, with a corresponding decrease in the recrystallisation range and the as-recrystallised grain-size (e.g. Figures 67 and 68).
The effects of the matrix grain-size and particle concentration can be explained as follows. Alloys with a very low concentration of second-phase particles will behave in a manner similar to that of solid-solution alloys. Decreasing the original grain-size will cause reductions in the recrystallisation times and temperatures, the range of recrystallisation and the final recrystallised grain-size by increasing the number of available nucleation sites (Figures 49, 50, 52, 53, 62).

As the number of particles is increased, the particle/matrix interfaces predominate increasingly as nucleation sites. Thus, the recrystallisation process becomes less sensitive to variations in the initial grain-size. The rate of nucleation will increase as the particle concentration increases and the lower will be the temperature (isochronally) or the shorter the time (isothermally) for the completion of recrystallisation. As there is a direct relationship between the number of viable nuclei and the number of recrystallised grains that are produced, particle-accelerated recrystallisation will lead to a fine, uniform final grain-size which decreases as the particle concentration increases. (Figures 52, 53, 55, 56, 62, 64, 67, 68, 74 and 77).

At still higher particle concentrations, the inter-particle spacing will be small enough to initially hinder, and finally prevent the formation of recrystallisation nuclei. In such cases, decreasing the particle spacing will cause an increase in the recrystallisation range and produce a less uniform, coarse final grain-size due to the slow growth of a small number of nuclei. (Figures 55, 64, 68, 74, 77 and 78).

In the present investigation, the following approximate values for the critical inter-particle spacings have been obtained from Figure 78: \( \Delta_A = 3 \) microns and \( \Delta_B = 1.8 \) microns. This is in good agreement with the values predicted by the Mould-Cotterill hypothesis. In particle-accelerated recrystallisation, a fine recrystallised grain-size, which becomes finer as the concentration of coarse particles is increased, has been obtained. When recrystallisation is retarded by the presence of fine particles, a coarse grain-size, which becomes larger as the number of particles is increased, has been obtained. (Figures 67 and 77).

Sundberg et al. (143) have also reported high recrystallisation temperatures
and a coarse final grain-size for those alloys containing small, stable particles. The $A_3$ values for these alloys have been calculated and lie between 0.07 and 0.09 microns. This is also compatible with the Mould-Cotterill hypothesis.

Figure 88 is a plot of some of Doherty and Martin's data (122) which shows that their fully recrystallised grain-sizes fall into two distinct categories, connected with either accelerated or retarded recrystallisation.

Figures 68 and 78 indicate that the nucleation rate is affected to a greater extent than the growth rate by variations in the inter-particle spacing. This is consistent with the findings for other two-phase aluminium-based alloys (122, 124). However, in the copper-silica system, it has been reported that nucleation and growth rates are affected by comparable amounts (123). This has been attributed to the high interfacial energy between the silica particles and the matrix (123).

Therefore, the present investigation confirms that the same second-phase can cause either acceleration or retardation of primary recrystallisation and that the important parameters are particle size and inter-particle spacing. The work also satisfies the mechanism of recrystallisation outlined by Mould and Cotterill (124) and represented schematically in Figure 34.

The effects of particle concentration on the annealing behaviour of cold-worked, two-phase aluminium alloys can, therefore, be represented as shown in Figure 89. The nucleation and growth rates are represented schematically as functions of the inter-particle spacing. Figure 90 illustrates the effect that changes in particle concentration have on the fully recrystallised grain-size.

For solid-solutions or at wide spacings ($A_C$), there are few nucleation sites and a coarse grain size is produced. As the number of particles increases towards $A_A$, the nucleation rate increases and finer grain-sizes are obtained. At $A_A$, impingement of the embryos occurs and this hinders nucleus formation. Decreasing the inter-particle spacing still further to $A_B$ causes further reductions in both the nucleation and growth rates. Fewer and fewer nuclei are formed and the particles interfere with their subsequent growth. Under these circumstances, a coarse grain-size is produced. At spacings below $A_B$, nucleation probably occurs only by a process of the type outlined by Beck and Sperry (77).
Fig. 89. Schematic representation of the influence of inter-particle spacing on nucleation and growth rates for cold-worked and annealed two-phase Al alloys.

Fig. 90. Schematic representation of the influence of inter-particle spacing on the fully recrystallised grain-size for cold-worked and annealed two-phase aluminium alloys.
4.2.3. Summary

Recrystallisation is enhanced by the present of coarse, widely spaced particles ($A_3 > 2$ microns). At closer spacings, the nucleation of new grains is inhibited or completely prevented ($A_3 < 1$ micron). In all cases, the growth of new grains is impeded by the presence of particles.

The initiation of recrystallisation at second-phase particles in iron has been demonstrated by English and Backofen (118), Antonione et al. (120) and Leslie et al. (108). Antonione et al. (120) found the effect to be greater for particles having larger dimensions. Recrystallisation has been shown to begin at coarse particles in aluminium by Mould and Cotterill (124) and Doherty and Martin (122). Hence, particle-accelerated recrystallisation is generally controlled by an increase in the nucleation rate, in association with a relatively unchanged growth rate, as the particle content is increased and the inter-particle spacing allows particle/matrix interfaces to be viable nucleation sites.

Retarded recrystallisation has been reported for two-phase alloys for which $A_3$ is of the order of a micron or less (126-144). In this case, the nucleation rate and the growth rate are both decreased as the particle concentration is increased, for spacings below which particle/matrix interfaces cease to be viable nucleation sites.

In cases where a range of dispersions has been studied, the alloys with the smallest spacings recrystallised with the greatest difficulty (112, 122, 139). For retarded alloys, a large as-recrystallised grain-size has been reported (122, 139, 143).
5. CONCLUSIONS

The recrystallisation behaviour of Al-Zr alloys has been shown to be a function of the alloy content, the size and concentration of $\text{Al}_3\text{Zr}$ particles, the original grain-size before the final deformation, and the final amount of deformation.

The addition of 0.02\% Zr in solid-solution raises both the 50\% recrystallisation temperature and the temperature for complete recrystallisation of super-purity aluminium. The grain-size of the solid-solution alloy decreases as the initial grain-size decreases and the amount of prior deformation increases.

For Zr additions above the maximum solid-solubility limit, two opposing effects on the annealing behaviour of aluminium have been obtained. For coarse, widely spaced particles, the recrystallisation process is accelerated both isochronally and isothermally, with the production of a fine, recrystallised grain-size. As the concentration of particles is increased, the final grain-size decreases. For fine, closely spaced particles, the recrystallisation process is retarded, with the formation of coarse final grain-size.

An increase in the initial grain-size retards recrystallisation by decreasing the number of grain boundary nucleation sites. The grain-size effect becomes less pronounced as the particle concentration increases, until, in high particle content alloys, there is hardly any effect on recrystallisation.

The recrystallisation process is accelerated by increases in the final amount of deformation with corresponding decreases in the recrystallised grain-size.

It has been shown that the nucleation rate influences the recrystallisation process to a greater extent than the growth process, as the nucleation rate is more sensitive to changes in the concentration of particles.

The experimental results and observations have been explained in terms of a mechanism based on the effect of second-phase particles on the formation and growth of recrystallised grains from a deformation sub-structure.
6. RECOMMENDATIONS FOR FURTHER WORK

A thorough investigation of the effects of particle size and shape on annealing behaviour would be informative. The present work has shown that particle size influences the recrystallisation process but only particles of the same morphology have been used. Alloys with a range of particle sizes and shapes could be produced by powder metallurgy or internal oxidation techniques. The influence of size and morphology on primary recrystallisation could then be studied.

It would be useful to define more closely the critical concentration of particles when particles cease to enhance recrystallisation but hinder the process. This could be achieved by producing more Al-Zr super-saturated solid-solutions of varying Zr contents, and precipitating fine particles from them.

The use of the electron microscope would be very useful for examining the deformed and recrystallised formation of the changes involved in a microscopy may be able to define particle-retarded and particle-accelerated
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Appendix - C.W. Corti, P. Cotterill and G.A. Fitzpatrick
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The evaluation of the inter-particle spacing, and its significance in relation to recrystallisation and strengthening in dispersion alloys.

by

C.W. Corti, P. Cotterill and G.A. Fitzpatrick

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Synopsis.

The paper outlines the various definitions and formulae which have been used to evaluate the inter-particle spacing in dispersion alloys, and discusses the basic relationships between them. Data is presented for a series of alloy structures containing particles with radii in the range 0.1 to 2 microns for volume fractions in the range 0.0001 to 0.10. This indicates that significant differences occur between the numerical values which result from the use of the various formulae, especially in alloys having low particle volume fractions. The possible interpretative significance of these differences is illustrated by means of a re-assessment of the recrystallisation characteristics of dispersion alloys, and comments are made about the influence of the spacing evaluation on the presentation of strengthening data.

1. Introduction.

It is well known that dispersed particles can have a considerable influence on the properties of metals: e.g. strengths are increased; recrystallisation can either be accelerated or retarded compared with a single-phase alloy having the same composition as the matrix of the dispersion alloy. The magnitude of these effects depends on the size and spacing of the dispersed particles. However, these parameters rarely have an absolute value, even in a single specimen, since the particles are rarely uniform in size, shape or distribution. In addition, the inter-particle spacing can be calculated on the basis of any one of several different
definitions and/or formulae each of which leads to a different numerical value in a given alloy structure.

Occasionally experimentally determined property values are presented solely in terms of their variation with the volume fraction of the dispersed phase, which, taken in isolation, is a statement of the alloy's overall composition rather than of its dispersion characteristics. Correlations of this type should be interpreted with caution since variations in the initial fabrication procedure may have created significant variations in the property-controlling parameters (particle shape, size and distribution, and matrix grain-size etc.) which are not revealed by an unqualified statement of the total volume fraction occupied by the dispersed phase.

The authors are investigating the recrystallisation of iron-based and aluminium-based dispersion alloys, and have encountered difficulty in appraising the literature on the subject. This arises partly from the variety of formulae which have been used to describe and evaluate the inter-particle spacing, in different investigations, and partly from the fact that in certain cases values of one or other of the controlling parameters are omitted, and the reported data does not permit their calculation: thus, general comparisons of behaviour in the various alloy systems are difficult to achieve.

The effect of dispersed particles on the recrystallisation kinetics of aluminium-based alloys has been quantitatively related to their inter-particle spacing by Doherty and Martin\textsuperscript{1,2}, and by Hould and Cotterill\textsuperscript{3}, and the latter have combined the two sets of data to postulate a mechanism of recrystallisation in such alloys. In each of these investigations a comprehensive set of dispersion data was reported and the inter-particle spacings were calculated by means of a formula proposed by Shaw et al\textsuperscript{4}. However, Underwood\textsuperscript{5} has shown that this formula is open to certain basic criticisms which do not apply to other formulae.
The purposes of the present paper are, firstly, to assess the applicability of the various definitions and formulae which have been used by different workers to describe and evaluate inter-particle spacings; secondly, to indicate the magnitude of the numerical differences which arise from the use of the various formulae, for a range of typical dispersions, and thirdly to illustrate the interpretative significance of these differences by means of a re-assessment of the data reported in the above-mentioned recrystallisation studies.

2. THE EVALUATION OF THE INTER-PARTICLE SPACING

2.1 General aspects

The general topic of stereology has recently been thoroughly reviewed by Underwood\textsuperscript{6,7}, and the following account deals briefly with those aspects which relate specifically to the evaluation of the inter-particle spacing in dispersion alloys. The various symbols which are used in this treatment are listed, with their definitions, in the appendix; they are also defined in the text on the first occasion on which they are used, subsequent use then being without further definition.

In practice the shape, size and distribution of dispersed particles are not ideally uniform, and of necessity the various formulae relate to "average" values of the relevant parameters. This does not lead to serious error in the quantitative description of microstructures provided firstly, that the particles are distributed randomly (as distinct from uniformly), and, secondly, that evaluations are based on a statistically significant coverage of representative samples. However, in those cases where particles are segregated or clustered in groups, it may be necessary to evaluate the various parameters (especially the inter-particle spacing), separately in each of the relevant regions of the microstructure.

In addition it is necessary to distinguish between the implications of the word random as it is applied, firstly, to the distribution of particles within the microstructure, and, secondly, to the distribution
of the lines and/or planes of section which are used to obtain the data from which the various parameters are evaluated.

In the general case of a random distribution of uniform spherical particles (of radius \( r \)) equations are available\(^5,6,8\) relating the particle volume fraction (\( F_v \)), the number of particles per unit volume (\( N_v \)), the number of particles per unit area on any plane section (\( N_A \)), and the number of particles per unit length of a line passing randomly through the structure (\( N_L \)). The principal equations are as follows:-

\[
N_v = \frac{\pi N_A^2}{4N_L} = \frac{N_A}{2r} \quad \ldots (1)
\]

\[
r = \frac{2N_L}{\pi N_A} = \frac{3F_v}{4N_L} \quad \ldots (2)
\]

and \( N_A = \frac{3F_v}{2\pi r^2} \quad \ldots (3)\)

In addition, the volume fraction of particles, of any shape, can be obtained rigorously from the plane of polish of a metallographic specimen by means of any one of the following ratios\(^5,6\):-

\[
F_v = \frac{A}{A_t} = \frac{L}{L_t} = \frac{N}{N_t} \quad \ldots (4)
\]

where \( A, L \) and \( N \) refer respectively to the areas, line lengths, and numbers of grid points over the particles (denoted by the suffix \( p \)) and over the total structure (denoted by the suffix \( t \)) in the examined surface.

There are two basic concepts of inter-particle spacing: namely, the mean free path (or distance) and the nearest neighbour distance. These are defined and discussed in the following sections, firstly for the general case of randomly distributed particles, and secondly, for particular cases of specifically defined uniform distributions.

2.2 Randomly distributed particles

2.2.1 The mean free path

The mean free path, or distance, (\( \lambda \)) has been defined by Fullman\(^8\) and McLean\(^9\). It is the average distance between particles along any random straight line in the structure. The formula for its evaluation
has been shown by Fullman to be based on the fact that the number of interceptions of particles by the test line is the same as the number of matrix areas which are intercepted. Thus, using the same notation as in the previous section, the lineal fraction occupied by the matrix is given, firstly, by $N_L$ and secondly, by $(1-\frac{L^0}{L})$. Equation (4) shows that this latter expression is equal to the volume fraction occupied by the matrix $(1-F_v)$. Hence, Fullman's formula for the mean free path is as follows:

$$\tilde{L} = \frac{1 - F_v}{N_L} \quad ................ (5)$$

This formula is valid for any particle dispersion structure, since its derivation involves no assumptions about the size, shape or distribution of the particles. Moreover, although it is defined in linear terms, and obtained from the plane of polish, the mean free path is a three-dimensional parameter since it is usually calculated as the average value from a series of random test lines on several random planes of polish.

Another useful parameter is based on the fact that the average random particle intercept centre-to-centre distance ($\sigma$) is given by the reciprocal of the number of particles intercepted per unit length of the test line (i.e. $1/N_L$). As Underwood has shown, this exceeds the mean free path (which is the corresponding edge-to-edge distance) by an amount which equals the average particle intercept length ($\bar{L}_3$): thus:

$$\bar{L}_3 = \sigma \lambda = \frac{1}{N_L} - \lambda \quad ................ (6)$$

substituting for $\lambda$, from equation (5) leads to the following expression:

$$\bar{L}_3 = \frac{F_v}{N_L} \quad ................ (7)$$

This parameter* ($\bar{L}_3$) represents a lineal measure of the effective intercept length.

---

*Footnote The average particle intercept length ($\bar{L}_3$) is the average length of any line passing through the particle, randomly, on any plane section. It differs, numerically, from the actual diameter of the projected, or sectioned, area of the particle, on the plane of section, although these two parameters are related mathematically. In the case of spherical particles the former is given by $4/3\pi$, whilst the latter is equal to $2r\sqrt{2/3}$, (see reference 6).
size of the particle in relation to its interception by a random test line. It is applicable to all dispersion structures since, once gain, no assumptions as to the particle shape, size or distribution are involved in the derivation. Substituting equation (7) into equation (5) leads to the following expression for the mean free path (\( \lambda \)) in terms of the particle intercept length (\( L_3 \)), and the volume fraction (\( F_v \)):

\[
\lambda = L_3 \left( \frac{1}{F_v} - 1 \right)
\]  

Although equations (5) to (8) have great generality, since they make no assumptions about the particle characteristics, the accuracy involved in the use of a single value of the mean free path to uniquely describe a given dispersion structure is, to some extent, distribution dependent. For truly random dispersions a series of test lines and/or planes taken from any one of the possible angles and orientations will have statistically equivalent particle distributions. Once, provided that sufficient measurements are made, the mean free path will have a single value whether it is measured, firstly, along a single line, secondly, as the average value for several lines on one lane, or thirdly, as the average value for several lines and planes throughout the structure as a whole.

The use of a series of test lines and/or planes in normal practice, therefore, arises from the need to ensure statistically representative overage of the structure. The resulting value of the mean free path will then be genuinely characteristic of the structure as a whole, and it should not be necessary to qualify its description by the use of the words "linear", "planar" or "volumetric" respectively. However, in the case of a dispersion in which the particles are distributed uniformly (as distinct from randomly) there will be anisotropic variations in the linear and planar mean free path values, which will
Underwood\(^{(6)}\) has given a series of formulae which enable the mean particle intercept length to be calculated from a knowledge of the particle geometry for a wide variety of different particle shapes. In the specific case of spherical particles, substituting equation (2) into equation (7) gives the following simple relationship between the mean particle intercept length \(\bar{L}_3\) and the particle radius \(r\): 

\[
\bar{L}_3 = \frac{4}{3} r \quad \dots \quad (9)
\]

Comparison of equations (8) and (9) shows that the mean free path \(\lambda\) is directly related to the volume fraction \(F_v\) and the radius \(r\) of spherical particles, as follows:

\[
\lambda = \frac{4}{3} r \left( \frac{1}{F_v} - 1 \right) \quad \dots \quad (10)
\]

2.2.2. The nearest neighbour distance

The nearest neighbour distance \(\Delta\) is usually defined as the average centre-to-centre distance between any particle and its nearest neighbouring particle. Two such distances have been described: one in the volume as a whole and the other on a plane section. Gurland\(^{(10,11)}\) has given formulae for these distances which are based on derivations by Hertz\(^{(12)}\) and Chandrasekhar\(^{(13)}\); the topic has been reviewed by Forscher\(^{(14)}\).

The formulae were originally derived for a randomly distributed array of points on the basis of the probability of finding the nearest neighbour at a distance between \(x\) and \((x + dx)\) from any point. They have since been applied to random dispersions of small separated particles, in which case the particle centres are assumed to replace the points in the original derivations. Using Underwood's notation\(^{(6)}\), the nearest neighbour distances in the volume \(\Delta_3\) and on a plane \(\Delta_2\) are given, respectively, by the following equations:
\[ \Delta_3 = 0.554 N_v^{-1/3} \quad \ldots \ldots \ (11) \]

and \[ \Delta_2 = 0.500 N_A^{-1/2} \quad \ldots \ldots \ (12) \]

In the specific case of spherical particles equations (1), (2) and (3) can be used to express these nearest neighbour distances in terms of the mean free path \( \lambda \), the particle radius \( r \) and the particle volume fraction \( F_v \), as follows:

\[ \Delta_3 = 0.554 \left( \frac{4}{3} \frac{x^2 \lambda}{1 - F_v} \right)^{1/3} \quad \ldots \ldots \ (13) \]

and \[ \Delta_2 = 0.500 \left( \frac{2}{3} \frac{x \lambda}{2 (1 - F_v)} \right)^{1/2} \quad \ldots \ldots \ (14) \]

Substituting for \( \lambda \) from equation (10) allows these expressions to be modified to relate the nearest neighbour distance to the particle radius and volume fraction only as follows:

\[ \Delta_3 = 0.554 \frac{x}{3} \left( \frac{4}{3} \frac{F_v}{x} \right)^{1/3} \quad \ldots \ldots \ (15) \]

and \[ \Delta_2 = 0.500 \frac{x}{3} \left( \frac{2}{3} \frac{F_v}{x} \right)^{1/2} \quad \ldots \ldots \ (16) \]

Analogous formulae can be derived for other particle shapes by the use of equations (11) and (12) in conjunction with Underwood's formulae for the mean intercept length of the appropriate particle geometry\(^{(6)}\). For example, Fitzpatrick\(^{(15)}\) has analysed the recrystallisation characteristics of a series of aluminium-zirconium alloys containing cubic and plate-shaped particles.

The assumption that the centres of finite-sized particles can be regarded in the same light as the infinitessimal points of the original analysis introduces an inherent error into the calculation of nearest neighbour distances. This arises since particle centres cannot be closer than a distance equal to twice their radius (i.e. \( 2r \)) since the particles cannot overlap. Hence, although the alloy may be one in which the distribution of particles is described as random (in the metallographic sense), the distribution of particle centres cannot correspond to the
assumption of randomly situated points (in the mathematical sense),
since this latter concept incorporates the possibility of point-
pairings at distances less than 2r.

It therefore follows that equations (11) to (16) are only strictly
valid when applied to point-particlers, although in practice, they are
not seriously in error when applied to dispersions of small particles
at low volume fractions (see also Section 2.4.2).

Bansal and Ardell(16, 17) have attempted to overcome this
deficiency by an analysis which takes into account the space occupied
by the particles in a random array of monodisperse spheres, and which
leads to the following expressions for the centre-to-centre nearest
neighbour distances in the volume (\(\Delta_3(BA)\)), and on a plane (\(\Delta_2(BA)\)),
respectively:

\[ \Delta_3(BA) = r \left\{ 2 + \frac{8F_v}{3 \frac{F_v}{V}} \cdot \left[ \frac{1}{3} \cdot \Phi_v \right] \right\} \quad \ldots \ldots (17) \]

and

\[ \Delta_2(BA) = \frac{11}{2} + \frac{1}{12F_v} \int_0^{6F_v} \frac{\left[ \frac{1}{3} \cdot x \right]}{\left( 6F_v - x \right)^{\frac{1}{2}}} \cdot e^{-x} \cdot dx \quad \ldots \ldots (18) \]

where the suffix (BA) is used to distinguish these expressions from those
based on the assumption of point-particlers (i.e. equations (11) to (16),
inclusive) and the \(\int ( )\) denotes an incomplete gamma function **.

It should be emphasised that strictly \(\Delta_2(BA)\) refers to the distance
between the centres of the circles formed by the intersection of the
spheres with the reference plane; this distance approximates to the
sphere centre-to-centre distance.

The errors involved in applying these equations to the real case
of a polydisperse particle distribution are likely to be small,

---

*Footnote: Bansal and Ardell described their particle distribution as
"uniform", but on the strict meaning of the terms used in this paper
it should be described as "random".

*Footnote: In order to permit easy calculation of the nearest neighbour
distances, Bansal and Ardell will supply tables of \(\frac{\Delta_3(BA)}{r}\) and
\(\frac{\Delta_2(BA)}{r}\) values on request.
specially when the particle size range is small. However, it should 
e be appreciated that Bansal and Ardell's equations were derived 
pecifically for a dispersion of spherical particles and they are not 
trictly accurate when applied to non-spherical particles.

Equations (11) to (16) relate to the mean centre-to-centre nearest 
eighbour distances. It is possible to evaluate the corresponding edge- 
o-edge nearest neighbour distances (denoted here by the symbol Z; with 
the appropriate suffix) by subtracting the mean particle diameter (2r) 
rom the values given by the above-mentioned equations, although it 
ould be noted that such an adaptation of formulae based on the 
ssumption of random particle distributions is rarely used in the 
terpretation of metallurgical data.

Thus, on the basis of the assumption of point-particles the 
edge-to-edge nearest neighbour distances (Z and Z2) are given by 

\[ Z_3 = \Delta_3 - 2r = r \left\{ 0.554 \left( \frac{4\pi}{3r^3} \right)^{1/3} - 2 \right\} \]  

\[ Z_2 = \Delta_2 - 2r = r \left\{ 0.500 \left( \frac{4\pi}{3r^3} \right)^{1/2} - 2 \right\} \]  

\[ Z_3(\text{BA}) = \Delta_3(\text{BA}) - 2r = r \left\{ \frac{8F}{3F_v} \right\} \]  

\[ Z_2(\text{BA}) = \Delta_2(\text{BA}) - 2r = r \left\{ \frac{1}{12F_v} \int_0^{\sqrt{2/3}} \left( \frac{1}{x} \right) e^{-x^2} dx - 0.8584 \right\} \]

It should also be noted that the nearest neighbour distance has 
ometimes been defined in terms of the average distance between any 
article and its nearest two, three or four neighbours (18). 
learly, the formulae which are used to evaluate these versions will 
iffer characteristically from equations (11) to (22) (which are all 
ased on the distance to the single nearest neighbour). In general, 
e more near neighbours that are taken into account the larger will be
resulting evaluated distance, since in a random particle array the
cond, third or fourth neighbours will be progressively further from the
reference particle than is the first (i.e. the nearest) neighbour.
3 Uniformly distributed particles
3.1 The description of the mean free path

The basic concept of a mean free path implies that its value should
independent of the direction of the line, or the orientation of the
ane section, on which it is measured. This situation is realised in
loys with random particle distributions (see section 2.2.1). However,
the distribution is geometrically uniform (as distinct from random),
may become necessary to distinguish between the linear, planar and
metric mean free paths, since there will be statistically significant
iations in the occurrence of particles on different test lines and/or
es, each of which will be characterised by its own particular mean
free path value.

In practice it is only possible to evaluate these various anisotropic
near and/or planar values if the measurement of data is carried out on
e basis of specifically oriented lines or planes, either in single
ystal specimens or within a single grain of a polycrystalline specimen.

In the case of randomly sectioned single crystals the lines and/or
es of measurement will have special geometric significance and the
ulting mean free path values will fall within the range of the
rious actual, orientation-dependent, linear and planar values within
structure. Similarly, for any plane-section, the use of a test line
ssing through several grains in a polycrystalline specimen will have the
statistical effect as would the use of several random lines, or
es, in a single crystal: i.e. it will lead to an average, rather than
pecific, value of the mean free path on that line or plane.

Hence, in a uniform particle array, the designated volumetric
me free path will represent an overall statistical average value
for the various lines and/or planes which are used to obtain the
original experimental measurements rather than a single value represent-
ing all possible directions and/or planes in the structure. Hence,
even if it is obtained by random sectioning and measurement, the
interpretative validity of the volumetric mean free path as a single
statement of the mean particle edge-to-edge distance will depend on the
extent to which the particle distribution differs from randomness.

2.3.2 The Shaw et al analysis of dispersion parameters

The analysis of dispersion parameters by Shaw et al (4) was
proposed in the context of an investigation of the tensile properties
of over-aged aluminium-copper alloys. It was assumed that the alloys
consisted of uniform spherical particles which were uniformly
distributed in the matrix, although it was stated that this assumption
was "only approximately in harmony with the (observed) microstructure".
However, as a consequence of this assumption the analysis was based on
the concept that the particles were located at the centres of uniform
spherical domains, each of which represented the volume of the particle
and its associated matrix.

On the basis of probability theory the average length of a random
test line was said to be equal to the domain radius, the reciprocal
of which therefore gives the number of domains which are intercepted by
a unit length of the test line. If this latter parameter is
multiplied by a factor representing the probability that a test line
will strike a particle (of radius $r$) in any domain (of radius $R$) the
resulting product gives the number of particles intercepted per unit
length of the test line. Shaw et al's formula for this number

$$N_L(S) = \frac{1}{R} \left\{ \frac{1}{1 - \sqrt{1 - (\frac{r}{R})^2}} \right\} \quad \ldots \ldots \ldots (23)$$

(N.B. Wherever possible the notation is the same as is used previously,
with the additional suffix (S) to denote that the symbol refers to the
version found in the Shaw analysis).
The reciprocal of the previous parameter equals the average random distance between particle centres \(\langle c(S) \rangle\), thus:

\[
\frac{1}{N_L(S)} = \sigma(S) = \frac{R}{1 - \sqrt{1 - \left(\frac{r}{R}\right)^2}}
\]

\[
\cdots \cdots (24)
\]

Shaw et al then stated that the volumetric mean free path \(\lambda(S)\) is given by the difference between the above distance and the particle radius, thus*:

\[
3(S) = \frac{R}{1 - \sqrt{1 - \left(\frac{r}{R}\right)^2}} - r
\]

\[
\cdots \cdots (25)
\]

or

\[
\lambda(S) = R \left\{ \frac{1}{1 - \sqrt{1 - \left(\frac{r}{R}\right)^2}} - \frac{r}{R} \right\}
\]

\[
\cdots \cdots (26)
\]

In addition, Shaw et al obtained the following formulae for the number of particles per unit area of a plane section \(N_A(S)\) and the ratio of the volume of a particle to the volume of its associated surrounding, matrix \(F_R(S)\) :

\[
N_A(S) = \frac{2x^2}{R^2}\cdots \cdots (27)
\]

and

\[
F_R(S) = \frac{x^3}{R^3 - r^3} = \frac{1}{(\frac{r}{R})^3 - 1}\cdots \cdots (28)
\]

Numerical values for these two parameters were obtained experimentally; the former by direct metallographic observation, and the latter from a knowledge of the alloy composition, the phase diagram and the phase densities. Hence, simultaneous solution of equations (24) and (25) produced values of the domain and particle radii \(R\) and \(r\), respectively) which were then used to evaluate the volumetric mean free path.

*Footnote - N.B. By analogy with Underwood's analysis of the mean intercept length for a random line within a spherical particle, the average length of a test line in domain or in a particle should be given by \(4/3R\) and \(4/3r\) respectively, and not simply by the radii (as stated by Shaw et al). Equations (23) to (26) should therefore be modified accordingly, although they are treated here in the form originally given by Shaw et al.
It should be noted that the above-mentioned volume parameter \( F_R(S) \) is a volume ratio and not a volume fraction. On the basis of Shaw et al's assumptions about the microstructure the volume fraction \( F_V(S) \) is given by the ratio of the volume of a particle to that of a total domain (including the particle), thus:

\[
F_V(S) = \left( \frac{r}{R} \right)^3
\]

Since the spherical domains are in mutual contact, with the particles at their centres, the inter-particle centre-to-centre nearest neighbour distance in a volume \( \Delta_3(S) \) is equal to the domain diameter \( 2R \). Re-arrangement of equation (24) allows this to be formulated, as follows:

\[
\Delta_3(S) = 2R = 2r \left( \frac{1}{F_V(S)} \right)^{1/3}
\]

In addition, Shaw et al suggested that the plastic properties of metals should perhaps be correlated with the mean free path between dispersed particles on a slip-plane. An equation for the planar mean free path was then derived in an analogous manner to that outlined above for the volumetric mean free path (equations (23) to (26)). It was assumed that the particles could be represented by circular sections at the centres of uniformly spaced circular domains on the appropriate planes. Consideration of intercept probabilities then led Shaw et al to the following equation for the planar mean free path \( \lambda_{P(S)} \) in terms of the circular particle and domain radii \( r' \) and \( R' \), respectively:

\[
\lambda_{2(S)} = \frac{2R'}{\text{arc sin} \left( \frac{r'}{R'} \right)} = \frac{4r'}{A}
\]

However, the numerical values which Shaw et al substituted into equation (31) in order to evaluate the planar mean free path were obtained from experimental measurements on random sections in polycrystalline specimens. Hence, the resulting evaluation should represent an average value for a number of crystallographically random
planes rather than a specific value for any particular plane (e.g. the slip plane). Hence, its value should be equal to that given by the formula for the volumetric mean free path (see also Section 2.3.1). However, the actual data reported by Shaw et al shows a considerable difference between the values of the mean free path obtained from equation (31) (the so-called "planar" value) and equation (26) (the so-called "volumetric" value). This suggests that there is a basic error at some point in the derivation of the above formulae.

As Underwood has pointed out (5) the basic concept of a spherical domain of uniform radius surrounding uniform spherical particles is difficult to justify, especially since the domains are not space-filling. Hence, the equations derived by Shaw et al will mis-represent the various parameters to an extent which reflects the values of the regions between the domains, even if it is assumed that the alloy consists of uniform spherical particles (of radius \( r \)) uniformly distributed (at a volumetric nearest neighbour distance of \( 2R \)) in a fully dense matrix. For example, equation (29) should be modified to become

\[
F_{v(S)} = k \left( \frac{r}{R} \right)^3
\]

where \( k \) is a factor which depends on the spacial arrangement of the domains: e.g. \( k = 0.74 \) if it is assumed that the domains are close-packed as, for example, in a face-centred-cubic array. However, the uniformity of particle shape, size and distribution, which is implicit in such a factorial modification of the Shaw analysis, still represents a special case when compared to the general one of randomly distributed, undefined, particles treated by Underwood (5-7) and Fullman (8) and discussed earlier.

2.3.3. Cubically distributed particles

Attempts have frequently been made to simplify the description of dispersion microstructures by assuming that the particles are distributed in a uniform cubic array. No specific formulae for the mean free path
are quoted for this structure although several workers have dealt with
the nearest neighbour distances.

Brown and Ham(19) have examined the planar analogue of a cubic
array and have shown that the centre-to-centre nearest neighbour distance
between particles which are arranged on a square lattice \(\Delta_{2(SL)}\) is
given by the following equation:-

\[
\Delta_{2(SL)} = N_A^{-\frac{1}{2}}(SL) \quad \text{...............(33)}
\]

where \(N_A(SL)\) is the number of particles per unit area of the square lattice.

In the case of a cubic array the number of particles per unit area
on a plane section and the nearest neighbour distance on that plane will
vary according to the orientation of the plane relative to the axes of the
cube. However, the nearest neighbour distance in the volume will always
be equal to the length of the edge of the distribution unit cube. This is
clearly equal to the nearest neighbour distance on plane sections which
 coincide with the cube face. Hence, equation (33) can be rewritten to
give the centre-to-centre nearest neighbour distance, in the volume, for
cubically distributed particles \(\Delta_{3(CL)}\) as follows:-

\[
\Delta_{3(CL)} = N_A^{\frac{1}{3}}(CL) \quad \text{...............(34)}
\]

where \(N_A(CF)\) is the number of particles per unit area on a plane section
lying specifically along the square faces of the cubic array.

Tyson(20) has modified equation (34) in order to evaluate the
corresponding edge-to-edge nearest neighbour distance \(\Delta_{3(CL)}\) by
subtracting a term which represents the average diameter of a particle
intercept area, on the test plane, in the specific case of spherical
particles (of radius \(r\)):-

\[
\Delta_{3(CL)} = N_A^{-\frac{1}{3}}(CF) - \frac{\pi r}{2} \quad \text{...............(35)}
\]

Substituting for \(N_A\) from equation (3) leads to the following alternative
formulae:-

\[
\Delta_{3(CL)} = r \left(\frac{2\pi}{3\sqrt{3}}\right)^{\frac{1}{3}} \quad \text{...............(36)}
\]

and
whilst substitution for \( N_A \) from equation (2) and then for \( N_L \) from equation (5) gives:

\[
\Delta_3^{(CL)} = \left\{ \frac{\pi r}{2(1-F_v)} \right\}^{1/2}
\]

\[
\text{and } Z_3^{(CL)} = \left\{ \frac{\pi r}{2(1-F_v)} \right\}^{3/2} - \frac{\pi r}{2}
\]

However, it should be noted that these substitutions assume that the fraction of particles on the distribution cube faces is the same as in the volume as a whole, which is not strictly valid. In addition, the edge-to-edge nearest neighbour distance should be measured along the line of the centres of the particles. It therefore follows that the term to be subtracted from the centre-to-centre nearest neighbour distance in equations (35), (37) and (39) should be \( 2r \), and not \( \frac{\pi r}{2} \) (as stated by Tyson). Hence, these equations will over-estimate the particle edge-to-edge nearest neighbour distance in a cubic array by a quantity which is equal to 0.43 times the particle radius.

Tyson has also pointed out that the initial term in equations (35) to (39) will be different for non-cubic arrays (e.g. for hexagonal arrays a multiplication factor of \( 2/\sqrt{3} \) is required): but he concludes that "the difference should be small and we can consider this (i.e. equation (35)) to be a reasonable approximation for a random array".

In practice, however, it must be acknowledged that equations (33) to (39) are highly specific formulae which were derived for a situation in which neither the particle distribution nor the planes of measurement are random. The initial term in these equations is derived on the basis that measurements are made specifically on planes of section which correspond to the faces of the assumed particle distribution unit cube (otherwise they do not give the centre-to-centre nearest neighbour distance). Variations towards random sectioning (by the use of several planes in a
single crystal, or of any section across several grains in a polycrystalline specimen) will inevitably lead to an anisotropic decrease in the number of particles observed per unit area compared with sections lying specifically along the distribution cube faces. Hence, they will produce misleadingly high calculated values of the nearest neighbour distances if the particles have a genuinely cubic distribution.

In addition, variations towards randomness in the particle distribution will lead to a decrease in the actual nearest neighbour distance since the displacement of a particle from a cubic lattice will inevitably place it closer to at least one of its original six symmetrically distributed nearest neighbours.

It is therefore to be concluded that despite Tyson's statement to the contrary equations (33) to (39) cannot have widespread application since their derivation presupposes a combination of particle distribution and specimen sectioning which rarely occurs in practice and which differs significantly from randomness.

2.4 Comparison of evaluations

2.4.1 Formulae for the nearest neighbour distance

The original formulae for the nearest neighbour distance (equations (11) and (12)) were based on the distribution of points, which represent particle centres, in an unrestricted random array, whereas Bansal and Ardell's formulae (equations (17) and (18)) take into account the fact that, in the real case, the particles cannot overlap and hence their centres are not strictly distributed in an unrestricted manner. However the former equations are more general than the latter since they make no assumptions concerning the particle shape whereas the latter are based specifically on a dispersion of spherical particles.

Hence, in view of their shape-independence the original derivations of the nearest neighbour distance, in the volume as a whole, (i.e. $d_3$) is used as a basis for comparison with other,
subsequent, derivations in the following discussion.

In general, the statistical chance of preparing a section such that the single nearest neighbour, to any reference particle, lies on that section decreases as the particle volume fraction decreases. Hence, the measured centre-to-centre nearest neighbour distance on a plane ($\Delta_2$ or $\Delta_2(^{BA})$) will tend to be greater than that in the volume as a whole ($\Delta_3$ or $\Delta_3(^{BA})$) to an extent which increases as the particle volume fraction decreases. Comparison of equations (16) and (15) leads to the following relationship between these distances, in the case of point particles:

$$\frac{\Delta_2}{\Delta_3} = 0.81 \left(\frac{1}{\phi_v}\right)^{1/6} \quad \ldots (40)$$

This relationship is illustrated in Fig. 1 (curve A) from which it can be seen that the two distances are approximately equal at high particle volume fractions, but that they differ to an increasingly significant extent as the volume fraction decreases.

The assumption of a uniform particle distribution is a geometric approximation which is made for analytical convenience but which rarely occurs in an actual microstructure. Hence, the substitution of experimental data obtained from a random microstructure into a formula based on the assumption of a uniform distribution will lead to numerical inaccuracies which are a reflection of the differences between the relevant formulae for the two types of distribution.

Comparison of equations (12) and (33) shows that the centre-to-centre nearest neighbour distance between particles arranged in a square lattice on a plane, ($\Delta_2(^{SL})$) is, on average, twice that which would be measured on any random plane in a structure containing randomly distributed point particles (i.e. $\Delta_2$). Hence, the use of the square-lattice formula will over-estimate the planar nearest neighbour distance,
in a microstructure having a random particle distribution, by a factor of 2 at all particle volume fraction values.

In the case of particles which are distributed volumetrically on a cubic lattice the centre-to-centre nearest neighbour distances on a plane and in a volume are equal, since in each case they are given by the length of the edge of the unit distribution cube. Hence, it follows, from equations (12), (34) and (40), that the centre-to-centre nearest neighbour distances in the volume for cubically distributed particles \( \Delta_3^{(CL)} \) and for randomly distributed point-particles \( \Delta_3 \) are related to the particle volume fraction, as follows:

\[
\frac{\Delta_3^{(CL)}}{\Delta_3} = \frac{2\Delta_2}{\Delta_3} = 1.62 \left( \frac{1}{v} \right)^{1/6}
\]

This latter relationship can also be obtained by comparing equations (36) and (15). However, it is only strictly accurate as a description of the two distributions if the particle volume fraction is measured on cube faces in the cubic distribution case (see also the discussion of equations (36) to (39) in section 2.3.3).

It therefore follows that the substitution of data from a random distribution microstructure into formulae based on the assumption of a cubic array of particles will overestimate the centre-to-centre nearest neighbour distance in the volume to an extent which increases as the particle volume fraction decreases, but which is independent of the particle dimensions. This is illustrated in Fig. 1 (curve B) for particle volume fractions in the range \( 10^{-7} \) to \( 10^{-1} \), from which it can be seen that the discrepancy is large at low particle volume fractions.

Curve C, in Fig. 1, shows that there is a similar trend in the corresponding ratio for the edge-to-edge nearest neighbour distances, in the volume \( \frac{\xi_3^{(CL)}}{\xi_3} \) as the particle volume fraction increases up to approximately 0.005. However, any further increase in particle content causes this ratio to increase to infinity, asymptotically, as the
particle volume fraction approaches 0.089. This latter trend arises because the calculated random distribution mean edge-to-edge nearest neighbour distance, in the volume, \( Z_3 \) becomes zero at this particle volume fraction on the basis of equation (17). Physically this implies that the particles would on average, be touching each other. This is structurally impossible, and it is an indication of the fact that the probability-based derivation of the initial random distribution formula (equation (11)) loses accuracy at high particle volume fractions*.

The various curves contained in Fig. 1 therefore suggest that the nature of a correlation between any property and the nearest neighbour distance will be of different forms, depending on the formula which is used to calculate the particular distance, especially if the data covers a wide range of particle content.

On the other hand, comparison of equations (30) and (15) shows that the centre-to-centre nearest neighbour distance in the volume calculated on the basis of the Shaw analysis \( \Delta_3(s) \) is 2.24 times that for randomly distributed particles \( \Delta_3 \) regardless of the particle size or content. In this case any correlation between a dispersion-dependent property and the nearest neighbour distance will be of the same basic form, apart from the multiplication factor, whether the spacing is calculated on the basis of the Shaw analysis or on the basis of a random distribution of particles.

2.4.2 Calculated data for typical alloys

In practice the inter-particle spacing is calculated in two stages.

*Footnote - Similarly, on the basis of equation (13), the calculated mean edge-to-edge nearest neighbour distance, on a plane, for randomly distributed particles \( Z_3 \) becomes zero at a particle volume fraction of 0.131.
Firstly, information obtained from direct metallographic observation is used to calculate the particle radius and the volume fraction by means of formulae such as equations (1) to (4), and secondly, these quantities are then substituted into one of the formulae discussed in sections 2.2 to 2.4 in order to obtain a value of the inter-particle spacing. Table 1 lists the numerical values which result from this procedure, on the basis of the various commonly used spacing formulae, for a series of hypothetical alloys containing spherical particles with average radii in the range 0.1 to 2.0 microns for volume fractions in the range $10^{-4}$ to $10^{-1}$. No assumptions are made as to the distribution of the particles; the data is therefore typical of that which occurs in a variety of investigations of dispersion-dependent phenomena in alloys having no specific type of particle distribution.

Examination of this data shows that the mean free path values are always greater than the nearest neighbour distances, for any particle content, regardless of the formulae which are used to evaluate these two basic forms of spacing. This is because, to a first approximation, the former is the average distance between any particle and all of its neighbours, whereas the latter is the average distance between any particle and its closest neighbour\(^{(11)}\).

The various nearest neighbour distances shown in Table 1 and Fig. 2 follow the trends and relationships discussed earlier (section 2.4.1). In particular the calculated values of the random distribution centre-to-centre nearest neighbour distance, in the volume ($A_3$) are less than the particle diameter ($2r$) at a particle volume fraction of 0.10 and the values arising from Bansal and Ardell's formulae for finite particles ($A_3(BA)$ and $A_2(BA)$) are significantly larger than those arising from the assumption of point particles (i.e. $A_3$ and $A_2$) at volume fractions greater than 0.001 and particle radii greater than 0.1 microns, the
extent of these differences increasing as either the volume fraction or the particle size increase.

In addition it is found that the values of the mean free path calculated on the basis of the Shaw analysis \( \lambda (S) \) are approximately 1.5 times those calculated on the basis of a random distribution of particles \( \lambda \) for a wide range of particle volume fractions. However, it should be noted that this ratio is obtained empirically from the calculated values and not fundamentally from the appropriate formulae owing to the nature of the Shaw analysis (see equations (25) and (26).

3. APPLICATIONS

3.1 Primary Recrystallisation

There is ample evidence that the rate of primary recrystallisation is accelerated (relative to that of the matrix phase alone) by the presence of widely spaced second phase particles\(^{(3,21-25)}\) and retarded by closely spaced particles\(^{(1,2,26-33)}\), although several different spacing evaluations have been used and few workers have published quantitative results for a wide range of spacings within a single alloy system.

The following points are considered relevant to the selection of an inter-particle spacing evaluation in the context of recrystallisation studies. Firstly, the formation of a nucleus is a three-dimensional process and, in the case of dispersion alloys, the controlling factor is likely to be the distance between a particle and its nearest neighbour, since this determines the uninterrupted volume of the matrix phase within which a nucleus may be formed. Secondly, nucleation often involves the re-arrangement of a deformation cell structure, the walls of which frequently pass through the particles in a dispersion alloy. It is therefore suggested that the interpretation of recrystallisation data should be based on interparticle spacing values which are calculated as the centre-to-centre nearest neighbour distance in the volume.

Doherty and Martin\(^{(1,2)}\) related the recrystallisation kinetics of
aluminium-copper dispersion alloys to the inter-particle centre-to-centre nearest neighbour distance, in the volume, calculated on the basis of the Shaw analysis ($\delta_3(0)$), since this had been developed during an investigation of the mechanical properties of similar alloys\(^4\).

Mould and Cotterill\(^3\) then used the same parameter to make a direct comparison of their results for aluminium-iron alloys (having wider inter-particle spacings, but for otherwise similar structural and experimental conditions) with those of Doherty and Martin.

This established that there are three distinct regions in the correlation between recrystallisation kinetics and the inter-particle spacing in dispersion alloys. Initially, the addition of particles to a single-phase matrix causes the rate of recrystallisation to be accelerated. This continues as the number of particles is increased, and the inter-particle spacing is decreased, until the spacing reaches a critical value ($C_1$, say), below which the rate of recrystallisation decreases as the spacing is decreased. Finally, there is a sudden intensification of the retardation process below a second, smaller, inter-particle spacing ($C_2$, say).

It is well known that the addition of widely spaced particles to a single-phase matrix leads to the formation of additional recrystallisation nuclei at the particle-matrix interfaces\(^{23,24}\) if the particle diameter is greater than $3000\sigma$\(^{34}\) (which was the case in the experiments referred to here). Mould and Cotterill utilised this observation to postulate, firstly, that the upper critical spacing ($C_1$) corresponds to a situation in which the mutual proximity of the particles has become such that an independent viable nucleus cannot be formed at each particle-matrix interface and, secondly, that the lower critical spacing ($C_2$) corresponds to a situation in which nucleation is virtually prevented at the particle-matrix interfaces and occurs only at a relatively small number of points in the alloy. They suggested that this latter situation would arise when
the inter-particle spacing was similar to, or less than, the deformation cell size; in which case the cell walls would be pinned by the particles and would therefore be unable to take part in the formation of a recrystallisation nucleus. They further showed that this hypothesis is consistent with the changes in the nucleation and growth rates which were observed in each of the various inter-particle spacing ranges.

The numerical values of the critical spacings reported by Mould and Cotterill (\(C_1 = 4.0 \mu m\) and \(C_2 = 1.8 \mu m\)) are larger than would be expected on the basis of the probable values of either (a) the minimum size of a viable nucleus, or (b) the deformation cell size, in these alloys. However, this discrepancy may arise from the errors which are involved in the use of the Shaw analysis, especially since the particles were distributed randomly (as distinct from uniformly) in the alloys in question. Moreover, if these spacings are re-evaluated* in terms of the centre-to-centre nearest neighbour distance, in the volume, for randomly distributed particles (\(\Delta_3\)) the lower critical spacing (\(C_2\)) is found to be 0.3 microns** (which is in good agreement with the generally observed cell size for the conditions), and the upper critical spacing (\(C_1\)) is approximately twice as large. These values are more consistent with the basic nature of the Mould-Cotterill hypothesis than the original values (calculated on the basis of the Shaw analysis).

Humphreys and Martin have reported that the time taken to attain 50 per cent recrystallisation increased smoothly as the inter-particle spacing decreased in copper-silica crystals\(^{(33)}\); this is shown in Fig. 3a.

---

*Footnote - This re-evaluation can be carried out either from the fact that \(\Delta_3 = 2.24 \Delta_2\) (see section 2.4.1) or by direct calculation from the dispersion data published in the original papers\(^{(11,3)}\).

**Footnote - This value is only slightly altered by the use of the Bansal and Lrdell evaluation, \(\Delta_3(BA)\).
In this case the inter-particle spacing was evaluated as the edge-to-edge nearest neighbour distance on the basis of a cubic distribution of particles \((\frac{\pi}{3}(CL))\), although the experimental evidence suggested that the actual distribution was random. However, the published data allows these spacings to be re-evaluated as the centre-to-centre nearest neighbour distance in the volume for a random distribution \((\Delta_3)\). If the results are plotted in terms of this spacing\(^{(35)}\) Fig. 3b, the shape of the curve is altered to indicate a two-stage retardation behaviour similar to that reported by Doherty and Martin for aluminium-copper alloys \((1,2)\).

It should also be noted that the time required for 50 per cent recrystallisation in the most widely spaced alloy \((\Delta_3 = 0.35\) microns) was significantly less than that for the unalloyed (matrix) copper, the value for which has been incorporated into Fig. 3b. Taken in conjunction with the re-evaluation of the spacing data this suggests that these alloys actually followed a three-stage acceleration and retardation sequence as a function of decreasing inter-particle spacings in the manner described by Mould and Cotterill although this is not indicated by Humphreys and Martin's original presentation of their results.

The re-evaluated inter-particle spacing at which the retardation process is intensified (i.e. \(C_2\) in the Mould-Cotterill hypothesis) is approximately 0.2 microns, whilst the reported deformation cell diameter for these alloys is approximately 0.3 microns. Unfortunately, it is not possible to evaluate the spacing at which the change from accelerated to retarded recrystallisation would have occurred (i.e. \(C_1\) in the Mould-Cotterill hypothesis) owing to the absence of data at wide spacings.

It is therefore suggested that the above re-assessment of published data, in alloys containing inter-metallic and ceramic particles, indicates that the form of the evaluation of the inter-particle spacing
can have a significant effect on the possible interpretation of experimental data in dispersion alloys, and also that it confirms the basic form of the Mould-Cotterill hypothesis which makes no assumptions concerning the nature of either the alloy matrix or the dispersed particles except that the particles should be relatively undeformable compared to the matrix.

### 3.2 Dispersion strengthening

In the early work on the mechanical properties of steels Gensamer et al.\(^{(36)}\) obtained a linear relationship between the 0.2% proof stress and the logarithm of the inter-particle mean free path in the ferrite. This has since been confirmed by several workers (e.g. Roberts et al.\(^{(37)}\), and Turkalo and Low\(^{(38)}\)). However, there has been no satisfactory theoretical interpretation of this empirical relationship.

Current theories attribute the strength of dispersion alloys to the influence of the particles on the movement of dislocations along the slip plane. For example, the widely accepted theory of Orowan\(^{(39)}\), for strengthening by relatively undeformable dispersed particles, suggests that the yield stress of a dispersion alloy is determined by the stress which is required to bow out a dislocation between particles: thus:

\[
\sigma_a = \sigma_m + \frac{4Gb_a}{l}
\]

where \(\sigma_a\) is the tensile yield stress of the alloy, \(\sigma_m\) is the tensile yield stress of the matrix phase, \(G\) is the shear modulus of the matrix phase, \(b\) is the Burgers vector of the glide dislocations, \(a\) is a factor associated with the glide dislocation line tension, and \(l\) is the inter-particle spacing.

The product \(4Gb_a\) can be determined experimentally as the slope of the line relating the tensile yield stress of the alloy to the reciprocal of the inter-particle spacing, whilst the intercept of such a line on the stress axis represents the basic yield stress of the
matrix phase alone.

It is generally agreed that in this situation the property-controlling spacing is the distance between the surfaces of the particles on the slip plane, and there has been much discussion as to how this spacing should be evaluated\(^{(18,33,39)}\). It was in this context that the square lattice formula (equation 33) was treated by Brown and Ham\(^{(19)}\) as being the planar analogue of a simplified particle distribution. This led to the development of the various formulae\(^{(19,40,41)}\) for the edge-to-edge nearest neighbour distance between particles distributed in a cubic array (i.e. \(\xi_3(\text{CL})\)).

Several workers have reported a linear relationship between the dispersion strengthening increment and the reciprocal of this particular spacing (i.e. \(1/\xi_3(\text{CL})\)), and thereby given support to the general form of the Orowan relationship in a wide variety of alloys\(^{(19,20,42,43)}\), although the extent of the agreement between the experimental and theoretical values of the slope of such lines varies appreciably. For example, Tyson\(^{(19)}\) made a re-evaluation of the combined data originally published by Roberts et al\(^{(37)}\) and Turkalo and Low\(^{(38)}\) and found a linear relationship between the yield stress and \(1/\xi_3(\text{CL})\) having a slope of 0.363 lb. per in., as compared with a theoretical value (for 4 G b a) of 0.320 lb. per in., in steels. In contrast to this Prasad et al\(^{(43)}\) obtained an experimental value for such a slope which was five times larger than the theoretical value when using the same cubic distribution evaluation for a series of nickel-zirconia alloys.

However, it should be appreciated that the above spacing evaluation \((\xi_3(\text{CL}))\) relates not only to a specific (cubic) type of particle distribution but also solely to the nearest neighbour distance on planes corresponding to the faces of the unit distribution cube, and not to the mean nearest neighbour distance on planes taken randomly within the structure. In
general, there is little evidence to suggest either that the particle
distribution in typical dispersion-strengthened alloys is cubic (as
distinct from random), or that the distribution on a slip plane is
specifically different from that on any other randomly selected plane.
Hence, it would seem reasonable to suggest that if a planar spacing is
to be used for the interpretation of dispersion-strengthening data it
should be evaluated as the mean edge-to-edge nearest neighbour distance
based on the assumption of a random particle distribution (i.e. \( Z \)).

It has been shown earlier that in the case of the centre-to-
centre nearest neighbour distance the assumption of a random particle
distribution leads to a value which is exactly half that calculated
on the assumption of a cubic array (e.g. compare equations (12) and (33),
or see data in Table 1 and Fig.1.). Within the limits of normal experi­
mental error the same ratio also applies to the corresponding edge-to-
edge distances calculated on the basis of the equations due to Hertz\(^{(12)}\)
(or Chandrasekhar\(^{(13)}\) and Tyson\(^{(20)}\) respectively, for particle
volume fractions less than \(10^{-3}\) (i.e. for typical dispersion strengthen­
ened alloys). Hence, experimental data which shows a linear relationship
between the yield stress and the reciprocal of the inter-particle spacing
evaluated on the assumption of a cubic distribution will also do so if the
spacing is calculated on the assumption of a random distribution. However,
in the latter case the slope of the curve will be half that in the former
case; which will be of significance in the precise interpretation of the
dislocation phenomena which are involved in the strengthening mechanism. For

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*Footnote* The cubic distribution formula subtracts \(4r/2\) from the centre-
to-centre nearest neighbour distance in order to arrive at the edge-to-edge
value, whereas the subtracted term should be \(2r\) since the latter distance
is measured along the line of the particle centres. However, the
difference between these two terms is of the order of \(0.1\%\) of the
calculated nearest neighbour distance for typical dispersion-strengthened alloy.

The limiting particle volume fraction value \(10^{-3}\) arises since
for greater particle contents the calculated value of the edge-to-edge
distance approaches zero, on the assumption of a cubic array, but does
not do so on the assumption of a random array (see Fig.1.).
example, in this case Tyson's re-evaluation of the data for steels would have a slope which is 0.57 times the theoretical value, whilst the corresponding ratio for Prasad's nickel-zirconia alloys would be approximately 2.1.

Finally, it should be noted that the formulae given by Hertz and Chandrasekhar for the centre-to-centre nearest neighbour distance on a plane (i.e. equations (12), (14) and (16)) were originally derived for the distance between randomly distributed points, which were taken to represent the centres of dispersed particles. Hence, they relate to the distance between the centres of pairs of particles the centres of which both lie on the plane of evaluation: and it follows that the formulae for the corresponding edge-to-edge distances (i.e. $Z_2$ in equation (20)) relate to the same pair of particles. However, in a random particle distribution there will generally be other closer particles which intersect the reference plane but which have their centres off this plane. Such particles will not be taken into account in the evaluation of the planar nearest neighbour distance on the basis of the assumption of point-particles (i.e. $\Delta_2$ or $Z_2$) yet their presence will have considerable relevance to the passage of dislocations along the reference plane.

This is illustrated in Fig.4, which shows that particles lying wholly outside the reference plane will not interfere with the passage of a dislocation on that plane. Hence, the relevant distance will be the distance between the edges of the nearest neighbours which actually intercept the plane (i.e. $Z_2^{(BA)}$) in the case of spherical particles. This will, in general, be less than the planar nearest neighbour distance evaluated on the basis of point particles (i.e. by equation (20)) but greater than that in the volume as a whole since the latter will include particles which are closer to the reference particle but which do not intersect the reference plane. However, reference to Table 1 and Fig.2 reveals a paradoxical situation in that evaluated $Z_2^{(BA)}$ spacings
tend to be larger than those of \(z_2\). This is probably a reflection of the errors that arise in the application of the point-particle calculation to finite-sized particles, eqn.(16) and which is discussed in section 2.2.2.

4. **CONCLUSIONS**

4.1 **Comparison of Formulae**

It has been shown that formulae based on the assumption of a random distribution of particles and formulae based on the assumption of uniform distributions lead to characteristically different values of the calculated interparticle spacing for any given alloy. In particular the following conclusions are drawn:

a) The evaluated Mean Free Path is always considerably greater than the evaluated Nearest Neighbour Distances in any structure.

b) The mean Nearest Neighbour Distance in a plane, \(\Delta_2\), is greater than that in the volume, \(\Delta_3\), by a factor which decreases as the particle volume fraction increases.

c) The Shaw et al analysis, which is based on the assumption of a uniform particle distribution, leads to evaluated Nearest Neighbour Distances in a volume which are 2.24 times larger than those calculated on the basis of a random distribution (\(\Delta_3\)).

d) The assumption of a cubic distribution of particles leads to evaluated Nearest Neighbour Distances which are twice as large as those calculated for plane sections in a random particle distribution (\(\Delta_2\)).

4.2 **Choice of Formulae**

The properties of dispersion alloys should be interpreted in terms of the appropriate interparticle spacings; the evaluation of the latter should be made on the basis of particle distributions that are in harmony with the observed microstructures. In general, random distributions are normally observed and therefore the Nearest Neighbour Distance formulae derived by Hertz \(^{(12)}\) and Chandrasekhar \(^{(13)}\) will be used, except where the particles are spherical. In this latter case the
derivations of Bansal and Ardell\textsuperscript{(17)} are more accurate.

4.2.1. **Recrystallisation Studies**

It has been concluded in Section 3.1 that the Nearest Neighbour Distance in a volume, centre-to-centre, ($\Delta_3$ or $\Delta_3(BA)$) is the most relevant spacing parameter.

4.2.2 **Dispersion Strengthening Studies**

Interpretation of dispersion strengthening in terms of dislocation mechanisms (Section 3.2) leads to the conclusion that the planar edge-to-edge Nearest Neighbour Distance ($\bar{\varepsilon}_2$ or $\bar{\varepsilon}_2(BA)$) is the most apt spacing parameter.

4.3 **Dispersed-phase Recrystallisation**

The re-evaluation of published data\textsuperscript{(1,3,33)} in terms of the appropriate interparticle spacings (calculated on the basis of a random particle distribution) is shown (section 3.1) to support the Mould-Cotterill hypothesis and indicates that the critical spacings are more in accord with predicted values compared to those of the original evaluations.
TABLE I  
Values of Interparticle Spacings for a Typical Range of Dispersion

Data Resulting from the Use of Standard Formulae

N.B. Particles are assumed to be spherical, Radii and Spacing values are in microns

(a) Edge-to-edge Spacings:

<table>
<thead>
<tr>
<th>Character:</th>
<th>Mean Free Path</th>
<th>Nearest Neighbour Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Fraction</td>
<td>in a volume or on a plane</td>
<td>on any plane</td>
</tr>
<tr>
<td>Particle Distribution</td>
<td>Random</td>
<td>Uniform</td>
</tr>
<tr>
<td>Particle Radius</td>
<td>Fullman\textsuperscript{8} (eq.10)</td>
<td>Shaw\textsuperscript{4} (eq.29)</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.1</td>
<td>1,333</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>6,666</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>13,332</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>26,664</td>
</tr>
<tr>
<td>0.001</td>
<td>0.1</td>
<td>133.2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>666.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1,332</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>2,664</td>
</tr>
<tr>
<td>0.005</td>
<td>0.1</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>132.7</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>265.4</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>530.8</td>
</tr>
<tr>
<td>0.010</td>
<td>0.1</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>66.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>132.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>264.0</td>
</tr>
<tr>
<td>0.050</td>
<td>0.1</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>50.7</td>
</tr>
<tr>
<td>0.100</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>24.0</td>
</tr>
</tbody>
</table>
(b) Centre-to-Centre Distances

<table>
<thead>
<tr>
<th>Character</th>
<th>on a plane</th>
<th>in the volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Distribution</td>
<td>Random</td>
<td>Random</td>
</tr>
<tr>
<td>Volume Fraction $F_v$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Radius, $r$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta_2$</td>
<td>$\Delta_3(BA)$</td>
<td>$\Delta_2$</td>
</tr>
<tr>
<td>$0.0001$</td>
<td>7.2</td>
<td>7.2</td>
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<td>36.2</td>
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<tr>
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<td>72.4</td>
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<td>144.7</td>
</tr>
<tr>
<td>2.0</td>
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<td>2.3</td>
</tr>
<tr>
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<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>0.5</td>
<td>11.5</td>
<td>11.7</td>
</tr>
<tr>
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<td>22.9</td>
<td>23.4</td>
</tr>
<tr>
<td>2.0</td>
<td>45.8</td>
<td>46.8</td>
</tr>
<tr>
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<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>0.1</td>
<td>5.1</td>
<td>5.4</td>
</tr>
<tr>
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<td>10.2</td>
<td>10.9</td>
</tr>
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<td>20.5</td>
<td>21.7</td>
</tr>
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</tr>
<tr>
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<td>0.72</td>
<td>0.79</td>
</tr>
<tr>
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</tr>
<tr>
<td>0.5</td>
<td>7.2</td>
<td>7.9</td>
</tr>
<tr>
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<td>14.5</td>
<td>15.8</td>
</tr>
<tr>
<td>2.0</td>
<td>0.32</td>
<td>0.41</td>
</tr>
<tr>
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<td>0.32</td>
<td>0.41</td>
</tr>
<tr>
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<td>1.6</td>
<td>2.1</td>
</tr>
<tr>
<td>0.5</td>
<td>3.2</td>
<td>4.1</td>
</tr>
<tr>
<td>1.0</td>
<td>6.5</td>
<td>8.3</td>
</tr>
<tr>
<td>2.0</td>
<td>0.23</td>
<td>0.33</td>
</tr>
<tr>
<td>0.100</td>
<td>0.23</td>
<td>0.33</td>
</tr>
<tr>
<td>0.1</td>
<td>1.1</td>
<td>1.7</td>
</tr>
<tr>
<td>0.5</td>
<td>2.3</td>
<td>3.3</td>
</tr>
<tr>
<td>1.0</td>
<td>4.6</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Fig 1. Ratio of Nearest Neighbour Distances as a Function of the Particle Volume Fraction
Fig. 2 The Variation of Interparticle Spacing Values with the Volume Fraction of Spherical Particles (of radius 0.5 \( \mu \text{m} \))

**Symbols:** as Appendix
Fig. 3 Variation of Time for 50% Recrystallisation with Interparticle Spacing.

(a) Original Data (Humphreys and Martin 33, 1966)
(b) Re-evaluated Data (Corti and Cotterill 35, 1972)
Fig. 4  Schematic Representation of Nearest Neighbour Distances in a Volume and on a Plane
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