The Characterisation of the Spatial Distribution of Reinforcement in Powder Metallurgy Route Al/SiC\textsubscript{p} MMCs and its Effect on their Processing and Properties

by

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ABSTRACT

Whilst thorough mixing between the two components of a PM route MMC can be achieved, a "necklace" structure can be observed in HIPped materials which leads to small scale inhomogeneities in the finally worked composites. The origins and effects of these inhomogeneities have been investigated for a number of PM Al-4wt%Cu - 20wt%SiC<sub>p</sub> MMCs. All MMCs exhibited edge cracks on rolling, whilst the unreinforced material did not. As the matrix:reinforcement particle size ratio tended towards unity the reinforcement became more uniformly distributed throughout the matrix so cracking at the edges became less severe and a higher reduction in thickness could be achieved by rolling before edge cracks began to appear.

Three techniques were developed to assess the quality of the spatial distribution of reinforcements in MMCs. The first technique is based on the measurement of the distribution of interparticle spacings of the reinforcement, and the second is based on the Dirichlet tessellation construction. The results showed that the widths of the interparticle spacing and Dirichlet cell size distributions are a function of the level of microstructural homogeneity. Both techniques are not sensitive enough to small variations in spatial distribution. The third technique is based on measurement of the variation in local energy dispersive X-ray (EDX) analysis. Computer simulation of idealised microstructures showed that it is possible to distinguish between random dispersions of different volume fractions, and between microstructures with clusters of different sizes and aspect ratios. Measurements from the real materials indicated that the technique is sensitive to small differences in the spatial distribution of the reinforcement and that it is a useful tool for measuring the quality of the microstructures.

DSC experiments of the HIPped composites showed that the temperature at which the θ' phase precipitated was a function of the matrix:reinforcement particle size ratio. As the microstructure of the materials became more homogeneous, the precipitation of the θ' phase occurred at lower temperatures, in the range 623K to 573K, than in the Al-4wt%Cu alloy and thus was accelerated. DSC experiments of the rolled composites showed a change in precipitation sequence in the MMCs with precipitation of the θ' phase occurring at the same temperature (T=573K) regardless of reinforcement particle size, and the precipitation of the θ" phase was suppressed.

The time required to reach peak hardness in the rolled composites under artificial ageing at 463K was not altered by the presence of the reinforcement. There was no direct correlation between the homogeneity of the distribution of the reinforcement within the matrix and the peak hardness. In MMCs with the same size of reinforcement a higher level of hardness was achieved when a smaller matrix mass median particle size was used.

The level of microstructural homogeneity affected the fracture properties of the composites. Notched tensile tests showed that the best indicator of notch sensitivity is the ratio of notched UTS to unnotched yield strength. A trend of rising notch sensitivity (diminishing toughness) with increasing matrix:reinforcement particle size ratio (increasing segregation of reinforcement) was observed. However, a possible reinforcement particle size effect makes the validity of this observation questionable.
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Abbreviations

CLSM  Confocal Laser Scanning Microscopy
CPH   Close Packed Hexagonal
CTE   Coefficient of Thermal Expansion
DIC   Differential Interference Contrast
DSC   Differential Scanning Calorimetry
EDX   Energy Dispersive X-ray
FCC   Face Centred Cubic
HIPped Hot Isostatically Pressed
HIPping Hot Isostatic Pressing
HPGA  High Pressure Gas Atomisation
MMC   Metal Matrix Composite
PM    Powder Metallurgy
SEM   Scanning Electron Microscopy/Microscope
SiC_p Silicon Carbide Particulate
SiC_w Silicon Carbide Whisker
TEM   Transmission Electron Microscopy/Microscope
UTS   Ultimate Tensile Strength
XMT   X-ray Microtomography
XRD   X-Ray Diffraction
VLS   Vapour-liquid-solid

Symbols

\[ a \]
Crack length, or numerical constant for the calculation of fracture toughness

\[ A \]
Structure dependent constant for calculating unit cell volume
Magnitude of burgers vector, or fraction of samples containing $k$ minor particles
Specific heat capacity of atomising gas
Specific heat capacity of metal
Reinforcement diameter, or droplet diameter
Diameter of major component particles
Diameter of minor component particles
Mass median particle diameter
Grain size, or diffusion coefficient of solute in the melt
Grain size controlled by grain growth
Grain size corresponding to one grain per particle
Young's modulus
Young's modulus of composite
Young's modulus of matrix
Young's modulus of reinforcement
The distance of the $i$th particle from its nearest neighbour
Volume fraction of minor component, or summation of the squares of nearest neighbour distances of all particles
Upper limit of volume fraction
Shear modulus of the matrix
Heat transfer coefficient
Intensity of segregation
Strain energy release rate
Number of minor particles, or constant in empirical grain size equation
Thermal conductivity of atomising gas
Thermal conductivity of matrix
Thermal conductivity of reinforcement
Hall Petch constant
Mode one plane strain fracture toughness
Interparticle spacing
Side length of square prismatic dislocation loops
Mixing Index
Total number of particles, or constant
\( N \)  
Number of samples, or total number of pairs of points, or strain hardening exponent

\( f(N) \)  
Function of the strain hardening exponent

\( N_f \)  
Number fraction of minor component particles

\( N_{\text{min}} \)  
Number of minor component particles

\( N_{\text{maj}} \)  
Number of major component particles

\( p \)  
Volume fraction of minor component

\( P_{\text{min}} \)  
Volume of a minor component particle

\( P_{\text{maj}} \)  
Volume of a major component particle

\( Q_{AB} \)  
Similarity coefficient between two correlograms, A and B

\( r \)  
Distance between two points compared for concentration, or radius of a small sphere

\( r_{\text{min}} \)  
Radius of minor component particles

\( r_{\text{maj}} \)  
Radius of major component particles

\( R \)  
Radius of a large sphere

\( R(r) \)  
Coefficient of correlation between concentrations at two points separated by a distance \( r \)

\( s \)  
Average inclusion spacing, or standard deviation of concentrations at all points

\( S \)  
Aspect ratio of the reinforcement, or measured standard deviation of the volume fraction of minor component in real samples

\( t \)  
Deformation zone size

\( T \)  
Tearing modulus, or temperature

\( T_{\text{melt}} \)  
Temperature of a liquid metal droplet

\( T_{\text{gas}} \)  
Temperature of atomising gas

\( \Delta T \)  
Change in temperature

\( \Delta T_e \)  
Equilibrium freezing range of alloy

\( dT_L/dx \)  
Temperature gradient in liquid metal

\( u \)  
Velocity of the atomising gas

\( V \)  
Solidification growth front velocity

\( V_f \)  
Volume fraction

\( V_m \)  
Volume fraction of matrix

\( V_r \)  
Volume fraction of reinforcement

- x -
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_a$</td>
<td>Volume fraction of $\alpha$ phase</td>
</tr>
<tr>
<td>$V_\beta$</td>
<td>Volume fraction of $\beta$ phase</td>
</tr>
<tr>
<td>$V_{\text{total}}$</td>
<td>Total volume of composite</td>
</tr>
<tr>
<td>$V_{\text{min}}$</td>
<td>Total volume of minor component</td>
</tr>
<tr>
<td>$V_{\text{maj}}$</td>
<td>Total volume of major component</td>
</tr>
<tr>
<td>$x$</td>
<td>Interparticle spacing</td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td>Mean interparticle spacing</td>
</tr>
<tr>
<td>$x^*$</td>
<td>Interparticle spacing in terms of number of standard deviations from the mean</td>
</tr>
<tr>
<td>$\bar{x}_{\text{min}}$</td>
<td>Mean volume fraction of minor component</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Volume fraction of minor component in the $i$th sample</td>
</tr>
<tr>
<td>$x_i'$, $x_i''$</td>
<td>Concentrations of the $i$th pair of points a distance $r$ apart</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Coefficient of thermal expansion, or coefficient of grouping, constant</td>
</tr>
<tr>
<td>$\alpha_{\text{comp}}$</td>
<td>Coefficient of thermal expansion of composite</td>
</tr>
<tr>
<td>$\alpha_m$</td>
<td>Coefficient of thermal expansion of matrix</td>
</tr>
<tr>
<td>$\alpha_r$</td>
<td>Coefficient of thermal expansion of reinforcement</td>
</tr>
<tr>
<td>$\Delta \alpha$</td>
<td>Difference in coefficient of thermal expansion</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Eshelby's accommodation tensor</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Linear strain, or cooling rate</td>
</tr>
<tr>
<td>$\epsilon_f$</td>
<td>Failure strain</td>
</tr>
<tr>
<td>$\epsilon_f^*$</td>
<td>Maximum strain acting at a crack tip</td>
</tr>
<tr>
<td>$\epsilon_c$</td>
<td>Constrained strain</td>
</tr>
<tr>
<td>$\epsilon'$</td>
<td>Stress-free strain</td>
</tr>
<tr>
<td>$\epsilon_{\text{th}}$</td>
<td>Thermal strain</td>
</tr>
<tr>
<td>$\epsilon_x$</td>
<td>Strain in the $x$-direction</td>
</tr>
<tr>
<td>$\epsilon_y$</td>
<td>Strain in the $y$-direction</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Distance between two points for which there is no correlation between the concentrations at the two points</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Cell size / secondary dendrite arm spacing</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of atomising gas</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson's ratio</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of atomising gas, or dislocation density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Standard deviation of interparticle spacings</td>
</tr>
</tbody>
</table>
\( \sigma_0 \)  Standard deviation of volume fraction of minor component in a completely segregated system
\( \sigma_r \)  Standard deviation of binomial distribution
\( \sigma_y, \sigma_0 \)  Yield stress
\( \sigma_{0.2\%} \)  0.2% proof stress
\( \sigma_{cy} \)  Composite yield strength
\( \sigma_{my} \)  Matrix yield strength
\( \sigma_{gb} \)  Grain size contribution to yield strength
\( \sigma_q \)  Strengthening due to dislocations
\( \sigma_o \)  Strengthening due to Orowan bypassing of reinforcing particles
\( \sigma_p \)  Strengthening due to Orowan passing of matrix precipitates
\( \sigma_i \)  Strengthening due to residual stress
\( \sigma_s \)  Matrix solute strengthening
\( \sigma_x \)  Stress in the \( x \)-direction
\( \sigma_y \)  Stress in the \( y \)-direction
\( \sigma_1 \)  Principal stress in the longitudinal direction
\( \sigma_3 \)  Principal stress in the transverse direction
\( \nu \)  Scale of segregation
\( \phi_1, \phi_2 \)  Volume (or area) fractions of regions of composition \( x_1 \) and \( x_2 \) respectively
\( \chi^2 \)  Value of the Chi square test for the comparison of distributions
Introduction

The research and development of metal matrix composites (MMCs) has been of major concern for only the past twenty-five years. In that time a large volume of literature has been published on the processing and performance of these materials. MMCs with ferrous and non-ferrous matrices combined with reinforcements in the forms of particulates, whiskers, and continuous fibres based on numerous ceramic systems have been studied. The MMCs with potentially the best properties are currently fabricated using the most costly routes from the most expensive raw materials, such as titanium alloys reinforced with boron or SiC monofilaments, produced for example by the hot pressing of matrix foils interleaved with layers of fibres. These materials have realised no large scale commercial success. MMCs based on cheaper aluminium and ceramic particulate raw materials have seen much greater application, and are being produced commercially on much larger production scales. Of these discontinuously reinforced aluminium MMCs, those fabricated by powder metallurgy (PM) routes have been studied most.

Processing has been recognised as the most important factor affecting the development and commercial success of MMCs. Furthermore, a particular problem has been recognised with the production of discontinuously reinforced MMCs. The
reinforcement has been found to segregate or cluster in the matrix rather than form a homogeneous dispersion. This occurs in MMCs produced via both liquid and PM routes. It is considered to be detrimental to the mechanical properties of the MMCs. For example, Davidson [1993] has shown that concentrations of strain occur in clusters of SiC reinforcing particles during tensile testing and suggested that this causes reduced ductility and fracture toughness. Until now the origins and effects of the spatial distribution of the reinforcement on these properties have not been investigated to any significant extent. Producers of PM route MMCs have attempted to reduce the clustering of reinforcements by using only the fine end (<45μm) of the matrix powder size distribution by sieving or gas classification, or by using a high energy blending stage, similar to mechanical alloying. The former has resulted in large amounts of unused over-sized matrix powder, and hence has increased the cost of the MMCs through both the extra processing step and the wasted powder. The latter also introduces an extra high cost processing step.

The present study attempts to address the problem of clustering of the reinforcement in discontinuously reinforced aluminium alloys, and in particular those fabricated by a PM route. By combining a number of Al-4wt%Cu alloy powders of different mass median diameters with SiC particulates (SiC\textsubscript{p}) of three different sizes, MMCs with varying degrees of inhomogeneously distributed reinforcement have been produced. The effect of the clustering of the reinforcement on the processing, heat treatment behaviour and mechanical properties of the materials has been investigated. In doing this, techniques for characterising the spatial distribution of the reinforcement were developed, thus formalising the description of the homogeneity of second phases in other systems.

The following strategy was adopted for solving these problems. Al-4wt%Cu powders were produced by high pressure gas atomisation. These were blended with 20wt%SiC\textsubscript{p}, hot isostatically pressed (HIPped), and hot rolled to form sheets of 2mm thickness. The microstructures of the MMCs in the HIPped and rolled conditions were characterised with particular reference to the spatial distribution of the SiC\textsubscript{p}. The mechanical properties of the rolled MMCs were measured by means of plain
Chapter 1. Introduction

tensile and notched tensile testing, whilst the response of the materials to precipitation hardening treatments were investigated by several techniques, hardness testing and differential scanning calorimetry (DSC) in particular.

The characterisation of the spatial distributions of SiC\textsubscript{p} was attempted by four methods. Firstly, this was done by considering local volume fractions of the SiC\textsubscript{p} by image analysis. Secondly, the local chemical analysis of the materials was measured. Thirdly, the distribution of interparticle spacings was found, and lastly a geometrical approach, the Dirichlet tessellation, was considered. The general applicability of these approaches will be discussed, along with the results for the materials specific to this study.

This thesis is structured in the following way. Chapters 1 and 2 consider the current knowledge relevant to this work. Chapter 2 is a review of previous literature on topics related to MMCs where general aspects of the classification, applications and production of MMCs are followed by a brief discussion of the effects of the reinforcement particle size and volume fraction on the physical, mechanical and recrystallisation properties of MMCs. The physical metallurgy of the Al-Cu system is briefly considered and the effects of reinforcement on the precipitation behaviour of the matrices of aluminium based MMCs are examined. Chapter 3 reviews current theoretical and practical aspects of mixture characterisation and their suitability for the description of second phase spatial distributions is addressed.

Chapters 4 to 11 describe the experimental work and findings of the present study. Chapter 4 gives details of all the experimental methods employed. Chapter 5 describes and discusses results of the characterisation of the raw materials from which the MMCs in this study were made. Chapter 6 discusses the development of the final as rolled microstructures of the MMCs during processing, and hence the origins of inhomogeneity of the dispersion of reinforcement in the powder route MMCs are described. Chapter 7 addresses the problem of formally characterising the spatial distribution of the reinforcement in these MMCs. The effect of the spatial distribution of the reinforcement on the formability and thermomechanical processing
of the MMCs is examined in chapter 8, whilst its effect on the mechanical properties of the MMCs is studied in chapter 9. Chapter 10 presents the conclusions drawn from experimental results, and the directions in which this work could progress in the future. Chapter 12 contains a number of appendices in which are reported the results of experiments allied to the main body of this study on the determination of optimum blending time and the characterisation of inclusions found in the MMCs, the computer programs written to aid the characterisation of spatial distributions of second phases are described, and the publications based upon this thesis are cited.
PART I

LITERATURE REVIEW
2.1. Classification of Metal Matrix Composites

MMCs can be classified in many ways, the most common of which are in terms of the matrix material, the reinforcement type, or the processing route. A number of production methods for MMCs will be discussed in a later section.

2.1.1. Selection of Reinforcement

Selection criteria for the ceramic reinforcement include:

- (i) elastic modulus,
- (ii) tensile strength,
- (iii) density,
- (iv) melting temperature,
- (v) thermal stability,
- (vi) coefficient of thermal expansion (CTE),
- (vii) size and shape,
- (viii) compatibility with matrix material, and
- (ix) cost.

Some selected properties of commonly used ceramic reinforcements are shown in table 2.1., [Ibrahim et al, 1991].
TABLE 2.1. Properties of selected ceramic reinforcements

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Density $(10^{-3} \text{kgm}^{-3})$</th>
<th>CTE $(10^{-6} \text{K}^{-1})$</th>
<th>UTS (MPa)</th>
<th>Stiffness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.98</td>
<td>7.92</td>
<td>221 (1363 K)</td>
<td>379 (1363 K)</td>
</tr>
<tr>
<td>SiC</td>
<td>3.21</td>
<td>5.40</td>
<td>---</td>
<td>324 (1363 K)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.66</td>
<td>$\leq 1.08$</td>
<td>---</td>
<td>73</td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>4.50</td>
<td>8.28</td>
<td>---</td>
<td>414 (1363 K)</td>
</tr>
<tr>
<td>WC</td>
<td>15.63</td>
<td>5.09</td>
<td>---</td>
<td>669 (297 K)</td>
</tr>
</tbody>
</table>

Reinforcements can be either continuous or discontinuous. Continuous reinforcements include boron, SiC and carbon fibres and Al$_2$O$_3$ refractory wools (e.g. Saffil fibre). Continuous fibres offer very high strengths and stiffnesses, but are expensive (approximately 600 $\text{kg}^{-1}$ for boron fibres [Ibrahim et al, 1991] and severely restrict secondary processing because of fibre damage and fibre to fibre contact. The properties of some continuous reinforcements are shown in table 2.2., [Bader, 1990].

Discontinuous reinforcements include carbides (e.g. SiC, B$_4$C), nitrides (e.g. Si$_3$N$_4$, AlN), oxides (e.g. Al$_2$O$_3$, SiO$_2$), or elemental materials (e.g. C, Si). These may be in the form of short fibres, whiskers, platelets or particulates. They offer good wear resistance and moderate increases in strength and stiffness, with the potential of ease of secondary processing. The relative costs of MMCs based on 6061-aluminium alloy with 10vol% loading of discontinuous reinforcements are shown in figure 2.1. The two lowest cost MMCs, reinforced with abrasive grade SiC and graphite powder, fall into the 3-5 $\text{kg}^{-1}$ range which makes them competitive with more conventional materials such as steels, non-ferrous alloys and fibre reinforced polymers.
### TABLE 2.2. Properties of continuous fibres for MMCs

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Diameter (µm)</th>
<th>Form</th>
<th>Stiffness † (GPa)</th>
<th>UTS † (GPa)</th>
<th>CTE (10⁻⁶ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C PAN Based</td>
<td>8</td>
<td>Continuous</td>
<td>230</td>
<td>4.5</td>
<td>-1.0 †</td>
</tr>
<tr>
<td>C Pitch Based</td>
<td>10</td>
<td>Continuous</td>
<td>725</td>
<td>2.2</td>
<td>-1.6 †</td>
</tr>
<tr>
<td>Boron</td>
<td>100</td>
<td>Single Fibre</td>
<td>480</td>
<td>3.5</td>
<td>8.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10</td>
<td>Continuous</td>
<td>75</td>
<td>6.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Al₂O₃ (DuPont)</td>
<td>20</td>
<td>Continuous</td>
<td>380</td>
<td>1.4</td>
<td>6.9</td>
</tr>
<tr>
<td>Al₂O₃ (ICI Saffil)</td>
<td>3</td>
<td>Staple</td>
<td>300</td>
<td>2.0</td>
<td>6.9</td>
</tr>
<tr>
<td>Al-Si-O</td>
<td>3</td>
<td>Staple</td>
<td>105</td>
<td>1.0</td>
<td>7.0</td>
</tr>
<tr>
<td>SiC</td>
<td>140</td>
<td>Single Fibre</td>
<td>430</td>
<td>3.5</td>
<td>4.9</td>
</tr>
<tr>
<td>SiC</td>
<td>13</td>
<td>Continuous</td>
<td>200</td>
<td>2.5</td>
<td>3.1</td>
</tr>
</tbody>
</table>

† Room temperature values

* Negative values of CTE indicate that the fibre contracts on heating

The structural efficiency of an MMC is a function of the density, elastic modulus, and tensile strength of the reinforcing phase. The chemical stability and compatibility of the reinforcements with the matrix material are important, not only for the end application, but also during material fabrication. The thermal mismatch strain, $\varepsilon_{th}$, between reinforcement and matrix is an essential consideration for composites that will be exposed to thermal cycling. $\varepsilon_{th}$ is a function of the difference between the coefficients of thermal expansion, $\Delta \alpha$, of the reinforcement and matrix

$$\varepsilon_{th} = \Delta \alpha \Delta T$$ ...

(2.1)
where $\Delta T$ is the temperature change. It has been proposed that relaxation of these strains, by the formation of a dislocation network, could alter the response of the MMC to thermomechanical processing relative to that of the monolithic alloys. The significance of these selection criteria will be discussed more fully in the relevant sections throughout the rest of this document.

2.1.2. Selection of Matrix

Matrices currently being investigated include ferrous alloys, and alloys based on the light metals - aluminium, titanium and magnesium. Interest has increased recently in the use of alloys based on intermetallic compounds such as titanium aluminides due to their enhanced stiffness and thermal stability. Rapidly solidified ferrous alloys are also being developed for the formation of in-situ MMCs based on fine dispersions of borides as the reinforcement [Baliga et al, 1994]. It is envisaged that these will be used for stiffness critical applications.

MMCs based on the light alloys have received much more interest. Of these those based on magnesium alloys have been studied the least. The main advantage of magnesium as a matrix for MMCs is its very low density. Iron is 4.5 times as dense, and even aluminium is over 1.5 times as dense as magnesium. Magnesium is also thought to exhibit better wetting characteristics when infiltrating fibres. Table 2.3 below [Polmear, 1989] shows the effect of the addition of SiC whiskers on the mechanical properties of magnesium alloy AZ31 (Mg-3Al-1Zn-0.3Mn).

<table>
<thead>
<tr>
<th>Material</th>
<th>Property at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Elastic Modulus (GPa)</td>
</tr>
<tr>
<td>AZ31</td>
<td>45</td>
</tr>
<tr>
<td>AZ31 + 10vol% SiC</td>
<td>69</td>
</tr>
<tr>
<td>AZ31 + 20vol% SiC</td>
<td>100</td>
</tr>
</tbody>
</table>

TABLE 2.3. Effect of SiC whisker reinforcement on magnesium alloy AZ31
The high specific stiffness and strength of titanium has been of interest to the aerospace industry for many years, and the material has become a candidate matrix for MMCs. Basic classes of titanium alloys available for MMC applications include the lightly alloyed alpha class (e.g., commercially pure Ti and Ti-5Al-2.5Sn), the intermediate alpha-beta alloys (e.g., Ti-6Al-4V), the metastable beta family (e.g., Ti-10V-2Fe-3Al, Ti-11.5Mo-6Zr-4.5Sn), the stable beta alloy class (e.g., Ti-30Mo), and the α₂ (Ti₃Al) and γ (Ti₅Al) aluminides [Smith and Froes, 1985]. Current fabrication processes use thin gauge foil (~0.13mm), and therefore alloys which can be easily fabricated to this form are required. The alpha alloys are of relatively low strength, unless aluminium levels are increased, in which case they are difficult to process. The stable beta alloys have attractive properties, but fabrication problems have negated their use. The alpha-beta and metastable beta alloy classes can be fabricated relatively easily. Fabrication problems of the Ti aluminides are still to be overcome. A major limitation to the introduction of titanium MMCs into service has been the degradation of strength of the materials due to the reaction of the matrix with the reinforcing fibres (mainly SiC), and this problem is now receiving much attention. The stiffness and UTS for a titanium based MMC and its unreinforced alloy are given below in table 2.4 [Smith and Froes, 1985].

**TABLE 2.4. Mechanical properties of an unreinforced and reinforced Ti alloy**

<table>
<thead>
<tr>
<th>System</th>
<th>Stiffness (GPa)</th>
<th>UTS at 293 K (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>120</td>
<td>890</td>
</tr>
<tr>
<td>Ti-6Al-4V/SiC (35vol%)</td>
<td>225</td>
<td>820</td>
</tr>
</tbody>
</table>

The matrix materials currently of most interest, especially for use with discontinuous reinforcements are the aluminium alloys. This is because they are cheaper than titanium, and hence their use with lower specification particulate reinforcements is
justified. Furthermore, their MMCs can be easily worked with existing practices with minor modifications. For MMCs produced via a liquid route the Al-Si casting alloys are preferred, although higher levels of Si than normal are used to reduce interfacial reactions (see section §2.3.3.). Powder route MMCs based on the 2xxx (Al-Cu-Mg), 6xxx (Al-Mg-Si), and 7xxx (Al-Zn-Mg) series alloys have been developed to a greater extent. These are all heat treatable alloys which can be hot worked in the single phase α-aluminium condition and then precipitation hardened either by natural (T4) or artificial (T6) ageing or by variations on these. The 2xxx and 7xxx series alloys have higher strengths, but the 6xxx series alloys have the advantage of being readily weldable. The mechanical and physical properties of aluminium alloys and MMCs produced with these alloys as matrix materials are given throughout the following sections.

2.2. Applications for MMCs

Metal matrix composites offer a number of key features which make them candidate replacements for many conventional materials in many applications. The main advantages offered by MMCs are:

(i) greater strength;
(ii) improved stiffness;
(iii) better high temperature properties;
(iv) improved wear resistance;
(v) lower coefficient of thermal expansion.

The relative benefit of each of these features varies depending upon the type of reinforcement used. Table 2.5 [Begg and Dolowy, 1991] summarises the relative importance of these advantages for a variety of reinforcements.
TABLE 2.5. Key properties offered by various MMCs by fibre classification

<table>
<thead>
<tr>
<th>Type of MMC</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength</td>
</tr>
<tr>
<td>Refractory Wool</td>
<td>1</td>
</tr>
<tr>
<td>Discontinuous</td>
<td>2</td>
</tr>
<tr>
<td>Continuous Fibre</td>
<td></td>
</tr>
<tr>
<td>(a) Graphite</td>
<td>2</td>
</tr>
<tr>
<td>(b) Other fibres</td>
<td>3</td>
</tr>
</tbody>
</table>

1 - Little Benefit  2 - Significant Benefit  3 - Major Benefit

A second major factor, besides performance, in determining the applications for a material is cost. It is not possible to give accurate costings for materials which are in the development stage, but table 2.6 [Begg and Dolowy, 1991] gives some broad estimates of price ranges for various materials based on a relative scale where the cost of the unreinforced metal is one. The cost effectiveness of the composite materials in a particular component application will not depend solely on raw material and primary processing costs. The total component price will also include secondary processing (e.g. extrusion, forging), finishing (e.g. machining, surface treatments) and often assembly (e.g. riveting, adhesive bonding) costs.
TABLE 2.6. Estimated relative price of MMCs

<table>
<thead>
<tr>
<th>Type of MMC</th>
<th>Price Range Relative to Monolithic Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractory Wool</td>
<td>1 - 3</td>
</tr>
<tr>
<td>Discontinuous:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Stir Cast</td>
<td>2 - 3</td>
</tr>
<tr>
<td>Powder Metallurgy</td>
<td>4 - 10</td>
</tr>
<tr>
<td>Whiskers</td>
<td>8 - 15</td>
</tr>
<tr>
<td>Continuous</td>
<td>20 - 250</td>
</tr>
</tbody>
</table>

2.2.1. Market Sectors

Trumper [1987] and Begg and Dolowy [1991] have reviewed the current applications of metal matrix composites. Since MMCs are a relatively new class of materials, many of these applications fall into the category of "prototype" or "demonstrator" components, with very few true production applications in present use. The principal market sectors which are currently looking to use MMCs are shown in table 2.7 [Begg and Dolowy, 1991], together with properties of the materials to be exploited. A small number of components have been produced for the automotive industry, but the inherent expense of most MMC materials and the investment in new processing technologies have been a stumbling block for large scale introduction of MMC components [Feest, 1988]. Most attention has therefore been placed on applications where cost is a less important issue, such as aircraft [Charles, 1990] (e.g. metal laminates for fuselage skins [Verbruggen, 1990], and engines [Wei, 1992]) and space applications [Dauphin et al, 1991].
### TABLE 2.7. The features of MMCs sought by various market sectors

<table>
<thead>
<tr>
<th>Market Sector</th>
<th>Materials Property Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Automotive engines</strong></td>
<td>Improved high temperature strength, fatigue and wear. Better match to CTE of steel</td>
</tr>
<tr>
<td><strong>Automotive others</strong></td>
<td>In certain components, e.g. brake callipers, stiffness.</td>
</tr>
<tr>
<td><strong>Aircraft engines</strong></td>
<td>Improved high temperature strength, creep resistance, stiffness.</td>
</tr>
<tr>
<td><strong>Aircraft airframe</strong></td>
<td>Improved strength and stiffness.</td>
</tr>
<tr>
<td><strong>Defence missiles</strong></td>
<td>Better high temperature strength, higher modulus.</td>
</tr>
<tr>
<td><strong>Defence armour</strong></td>
<td>Complex high strain rate properties.</td>
</tr>
<tr>
<td><strong>Defence tank tracks</strong></td>
<td>Lower density, higher wear resistance.</td>
</tr>
<tr>
<td><strong>Defence torpedoes</strong></td>
<td>Higher modulus and strength.</td>
</tr>
<tr>
<td><strong>Space satellites</strong></td>
<td>Lower (zero) CTE, higher stiffness, self damping characteristics.</td>
</tr>
<tr>
<td><strong>Space Strategic Defence Initiative (SDI) space planes</strong></td>
<td>Higher thermal conductivity with high temperature strength.</td>
</tr>
<tr>
<td><strong>Space</strong></td>
<td>Higher strength at temperature and low density.</td>
</tr>
<tr>
<td><strong>Electronics substrates</strong></td>
<td>Matched CTE of ceramic at lower density.</td>
</tr>
<tr>
<td><strong>Sporting Goods various</strong></td>
<td>Higher stiffness, strength and high tech. image.</td>
</tr>
</tbody>
</table>

#### 2.2.2. Discontinuously Reinforced Aluminium

A number of aluminium alloys with discontinuous reinforcements are now on the market. They are relatively cheap MMCs (table 2.6) since the reinforcement is often an abrasive grade particulate, and they can undergo similar secondary processing to
the unreinforced materials. BP Metal Composites Ltd have produced a number of powder metallurgy route MMCs based on the 2124, 8090 and 6013 aluminium alloys [BP Metal Composites product data sheets]. These can be obtained in the form of rolled sheet or plate, forgings, or extrusions. BP Metal Composites have also produced a number of specific components. They have produced a superplastically formed aircraft door in collaboration with British Aerospace, Warton. Examples of forged components are missile control fins, inertial guidance system components and a formula 1 gear selector fork. They have produced extrusions including T-sections, I-sections, round bars and tubes, and a number of extrusions have been combined to produce aircraft instrumentation racking. In the USA the Advanced Composite Materials Corporation produce a number of SiC_w and SiC_p reinforced aluminium alloys, known as SXA® composites, based on 2xxx and 6xxx series alloys [Walker and Geiger, 1989]. The SXA® materials are classified into three grades - Structural, Electronic, and Instrument and Optical. A structural grade, high purity 2124 alloy reinforced with 15vol% SiC_w SXA® material has been used to make the skins and intercostals for two full-scale vertical tails of an advanced aircraft. Electronic grade 6061 alloy reinforced with SiC_p is being evaluated for hermetic microcircuit packages. Optical grade SXA® composites have been used for the tubular and plate supports (6061-20vol%SiC_w), and the secondary mirror substrate (2124-30vol%SiC_p) for an ultralightweight telescope. An early production application for instrument grade SXA® composites was for component covers of a missile's inertial guidance system, to replace the original expensive beryllium parts.

Duralcan USA, produce cylinder liners cast from low cost aluminium matrix composites, which offer the potential to reduce weight and improve performance in aluminium engine block systems [Hunt and Horgan, 1992]. The CTE of the composite more closely matches that of both the aluminium alloy pistons and the surrounding aluminium block than the more conventional grey cast iron. Its higher thermal conductivity enhances the transfer of excess heat from the combustion cylinder into the cooling system. The Lanxide Corporation produce developmental automotive brake rotors and callipers from SiC_p reinforced aluminium. The callipers, weighing 50% less than present nodular cast iron designs can be inserted into the same wheel
space without loss of braking performance [Hunt and Horgan, 1992].

Several other applications are either in production or under consideration [Begg and Dolowy, 1991]. For example "U" shaped channel extrusions of particle reinforced aluminium have been used by Lockheed for an instrument rack of a military aircraft. During high G-force turns unreinforced aluminium racks were not stiff enough. Carbon-epoxy racks were tried, but they had to be clad with aluminium to provide an earth path. The cladding gave rise to maintenance problems and added weight. The MMC proved cost effective and saved weight. In the defence industry discontinuously reinforced aluminium is under consideration for stiffness critical parts such as missile fins and torpedo bodies, and also for tank tracks to reduce weight. Bicycle frames and wheel rims are also being developed for their weight savings, and the high wear resistance of these materials is being utilised in horse shoes. Another sporting application has seen the use of the largest single pieces of MMC to date. These were the cross booms of an American catamaran which were extruded tubes, approximately nine metres long with a diameter of forty five centimetre.

2.3. Production of MMCs

There are a large number of production methods for metal matrix composites, which have been developed either from the conventional processing routes of unreinforced materials, or out of the need to make composites without damaging or rearranging the reinforcement. Continuous fibres may exhibit very little damage tolerance and some are too stiff to be draped or manoeuvred into dies or moulds. This therefore resulted in a need to develop completely new processing techniques, which has contributed to the high costs of continuously reinforced MMCs. These new processes include laying up arrays of fibres between foils of matrix material and hot pressing; spraying or vapour depositing matrix material onto single fibres and then consolidating them; and alternating layers of matrix powder and fibres followed by consolidation.
The total number of production methods for MMCs is far too large for all of them to be discussed here. This section will concentrate briefly on the fabrication of discontinuously reinforced MMCs only. The techniques by which these materials are made fall into a number of categories:

(i) In-situ MMCs,
(ii) Electro-forming of coatings,
(iii) Liquid route MMCs,
(iv) Two phase route MMCs,
(v) Powder route MMCs,
(vi) Mechanical alloying.

For each of these categories an example of a typical material will be given.

2.3.1. In-situ MMCs

Composite materials based on a pure aluminium matrix reinforced with sub-micron TiB₂ particles formed in-situ have been produced by Ma et al [1992]. They are produced by heating hot pressed mixtures of Al, Ti and B elemental powders above 973K (700°C) for ten minutes. This causes an exothermic chemical reaction between Ti and B to form fine particles of TiB₂. The precipitates form as block-like crystals which are free of structural faults. The interface between the TiB₂ particles and the aluminium matrix is clean and interfacial bonding is very strong. Ma et al reported also the presence of Al₃Ti precipitates. A comparison of the strengths of pure aluminium, Al/TiB₂ composites, and conventional discontinuously reinforced aluminium, at a variety of temperatures, is shown below in table 2.8 [after Ma et al, 1992].
TABLE 2.8. Comparative strengths of Al based MMCs at varying temperatures

<table>
<thead>
<tr>
<th>Material</th>
<th>Ultimate Tensile Strength (MPa) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room Temp</td>
</tr>
<tr>
<td>Pure Al</td>
<td>105</td>
</tr>
<tr>
<td>Al/15vol%SiC_p</td>
<td>195</td>
</tr>
<tr>
<td>Al/20vol%SiC_w</td>
<td>280</td>
</tr>
<tr>
<td>Al/15vol%TiB_2</td>
<td>350</td>
</tr>
</tbody>
</table>

The in-situ TiB₂ reinforced composite has over three times the room temperature strength of pure aluminium and is 1.8 times stronger than aluminium reinforced with a similar volume fraction of SiC particulate. The in-situ composite also has excellent thermal stability. It is still stronger at 573K (300°C) than pure aluminium at room temperature. The major drawback of the composites at present is the lack of control over the chemical reaction which forms the reinforcement.

2.3.2. Electro-forming of Coatings

Poeton [1988] has reviewed a number of composite coating systems which are developments of electrolytic, electroless and anodizing processes, which engineer improved lubricity, wear and corrosion resistance into a surface. Early examples include Tribomet T104C from BAJ Ltd, comprising fine inert ceramic particles into a matrix of electrodeposited cobalt for improved wear resistance, and Niflor from A T Poeton, which incorporated PTFE particles into an electroless nickel deposit for improved lubricity.

A more up to date electrodeposited coating is Elnsil (A.T. Poeton) which is a SiC/Nickel composite currently being applied to the cylinders of high performance motorcycles, chain saws and stationary engines. The coatings offer good oil retention properties with improved wear resistance. Tufram is an anodic composite coating.
formed by first growing a porous Al₂O₃ layer on aluminium by anodising. The pores are then impregnated by fluorocarbon polymers under controlled conditions. The resulting polymeric/ceramic coating is harder than steel, and exhibits excellent wear, corrosion and friction properties.

2.3.3. Liquid Route MMCs

Processing of discontinuously reinforced aluminium MMCs via a liquid route can be split into two categories. The first includes stirring of the reinforcement into the liquid matrix followed by conventional casting. The second includes the infiltration of a preform of fibres or particulates with the liquid matrix under pressure (e.g. vacuum infiltration, pressure infiltration, squeeze casting).

A number of approaches have been utilised to introduce up to a maximum of 20vol% of the ceramic particulates into the alloy melt [Rohatgi et al, 1986]. These include:

i) injection of powders entrained in an inert carrier gas into the melt using an injection gun;

ii) addition of particulates into the molten stream as it fills the mould;

iii) addition of the particulates into the melt via a vortex generated by mechanical agitation;

iv) addition of small briquettes, of co-pressed alloy powder and ceramic particulate, into the melt followed by stirring;

v) dispersion of the particulates in the melt by using centrifugal acceleration;

vi) pushing of the particulates in the melt by using reciprocating rods;

vii) injection of the particulates into the melt which is under ultrasonic agitation;

viii) zero gravity processing.

Some problems have been encountered in materials processed by conventional casting. Quality control of the castings in terms of dimensional tolerance has been identified as a particular problem [Kaufmann et al, 1992], due to altered shrinkage properties during solidification caused by a change in the coefficient of thermal
expansion of the MMCs. Agglomeration of the ceramic particulates during agitation, the settling of particulates, and the pushing of particulates by the growing dendrites have led to inhomogeneous distributions of the reinforcement and therefore to material unreliability. To overcome these problems the infiltration techniques have been developed.

A schematic of the infiltration process is given in figure 2.2. Infiltration techniques have been described by Mykura [1991], of which the process in figure 2.2 is typical. The preformed reinforcement (≤30vol%) is loaded into the die at the start of the cycle. The preform can be preheated 773-1273K (500-1000°C) to facilitate infiltration, and the die is heated 773-923K (500-650°C) to prevent chilling of the melt during injection. The melt is superheated by 100-200K above its liquidus. Once the preform is in position both the die cavity and pressure vessel are evacuated to remove air that would otherwise become trapped in the preform during infiltration causing porosity in the final material [Fujita et al, 1987]. When the preform is at the optimum temperature and vacuum, the gas pressure can be applied to the surface of the melt reservoir forcing liquid metal up the feed tube and into the die cavity to infiltrate the reinforcement. After complete solidification of the casting the pressurising gas is vented from the system allowing the melt in the feed tube to fall back down to the melt reservoir. The die can then be opened to eject the casting.

Clyne [1987] notes that it is possible for short fibres to be damaged under the infiltrating pressure. It is also possible that the binder required for ease of handling of the preform may form detrimental inclusions.

There are two major problems encountered when processing MMCs through the liquid route. The first is the inability of the molten aluminium to fully wet the reinforcement which potentially leads to porosity or poor interface strength. The addition of reactive elements such as Li, Mg, Ca, Ti, Zr, and P to the aluminium matrix improves the wetting characteristics through (a) a reduction of the surface tension of the melt, (b) a reduction of the solid-liquid interfacial energy, or (c) by inducing a chemical reaction at the interface. The second problem is the reaction of
the melt with the reinforcement to form embrittling phases either as a continuous layer or isolated precipitates [Lee et al., 1988]. SiC reacts with molten aluminium according to the reactions

\[
4\text{Al} + 3\text{SiC} \rightarrow \text{Al}_4\text{C}_3 + 3\text{Si}
\]

and

\[
4\text{Al} + 4\text{SiC} \rightarrow \text{Al}_4\text{SiC}_4 + 3\text{Si}.
\]

The aluminium carbide / SiC interface is generally rough [Teng and Boyd, 1992] and can lead to regions of stress localisation. This can lead to the failure of the interface, the aluminium carbide or the reinforcement. The voids formed due to this cause premature failure of the MMC. The extent of the interfacial reaction can be partially controlled either by increasing the Si content of the liquid matrix thus shifting the equilibrium to form lower concentrations of the carbides [Alonso et al., 1992], or by preoxidising the reinforcing particles [Teng and Boyd, 1992]

2.3.4. Two Phase Route MMCs

The following two techniques incorporate the ceramic particulate reinforcement into the metal matrix whilst the matrix is in a semi-solid state. In the first, known as compocasting, the ceramic particulates (≤20 vol%) are added to the matrix at a temperature within the solid-liquid range of the alloy, followed by vigorous agitation to form a low viscosity slurry. This vigorous agitation breaks up solidifying dendrites which would push the reinforcement into aggregates if they were allowed to grow, as in conventionally cast MMCs. This aids the distribution of the reinforcement, but does not avoid the problems of interfacial reaction.

The second two-phase route to forming MMCs was introduced by ALCAN as a modification of the "Osprey" spray deposition process [Willis, 1988, White et al., 1988]. The process is shown schematically in figure 2.3. The alloy to be sprayed is melted by induction heating in a crucible. The crucible is pressurised and the melt is ejected through a nozzle into an atomiser where the liquid stream is broken up into droplets by a number of pressurised gas jets. The particulate reinforcement (≤15 vol%) is injected into the cone of atomised droplets under controlled conditions.
The solidifying droplets and reinforcement are collected on a substrate placed in their line of flight, and a solid deposit is built up. The oversprayed powder is collected via a cyclone. The overspray mixture of Al alloy powder and SiC\textsubscript{p} poses a serious threat to the economics of this processing route and until solutions are found for the recycling or usage of the overspray the production costs will remain high. The deposited billet can undergo secondary working such as extrusion or forging. Warner \textit{et al} [1988] claim a cleaner ceramic-metal interface than that obtained by any other route involving the liquid matrix, although reaction products are still present. Solidification on the scale of droplets prevents the macrosegregation of alloying elements that would occur in full scale castings.

\subsection*{2.3.5. Powder Route MMCs}

The powder metallurgical route for the production of particulate reinforced MMCs was developed to overcome the problems associated with the liquid or semi-liquid routes. Contact between the matrix and reinforcement is induced by pressure and deformation of the matrix, and no longer requires the melt to wet the reinforcement. Porosity caused by lack of wetting is therefore eliminated. The phase equilibria between Al, Si and C indicate that the aluminium carbides cannot form at the temperatures used for processing of PM route MMCs (\textasciitilde500°C) when the C concentration is equal to or less than the Si concentration. The interfacial reactions between the reinforcement and liquid aluminium observed in the liquid route MMCs do not occur in the PM route materials. The toughness of MMCs produced in the solid state is therefore superior to that of the liquid route materials.

The PM process is shown schematically in figure 2.4. Firstly, the reinforcement is dried and sieved to deagglomerate the particles. The reinforcement (\textasciitilde40vol\%) is then blended with the matrix metal powder, usually gas atomised material, to obtain a homogeneous mixture of matrix and reinforcement. Gas atomisation for the production of powders and associated rapid solidification phenomena in general are discussed in section §2.4. Although dry blending is more usual, Bhanuprasad \textit{et al} [1991] suggest that the use of a polar solvent such as n-butanol as a blending medium is effective in deagglomeration and dispersion of SiC reinforcements. The blend is
then cold compacted and vacuum degassed. During degassing any adsorbed gaseous species are desorbed depending on the temperature of the degassing treatment. Billets are then fully consolidated. This can be achieved by hot pressing or hot isostatic pressing (HIPping). Sivakumar et al [1992] have reported a novel method of explosive compaction, which involves surrounding a metallic can containing the blend with an explosive, which after detonation sends a shock wave through the can collapsing it and causing compaction of the blend. The solid billets then undergo some secondary forming such as forging, rolling or extrusion.

An added benefit of the PM route is that the benefits of rapid solidification (RS) could be utilised in MMCs, such as finer microstructures and reduced segregation in the matrix. These benefits are discussed further in section §2.4.1. The most important of these, however, is the extension of solid solubility and the formation of thermally stable non-equilibrium phases which allow the production of alloys which could not be produced by any conventional method. In particular, Raghunathan et al [1992] have highlighted the Al-Fe and Al-Cr systems which have the potential to compete with titanium on a specific strength basis for light weight applications at temperatures between 523K (250°C) and 623K (350°C). The benefits of RS are not always considered however. The gas atomisation process is used by some manufacturers solely to produce good quality powders for secondary processing. This is certainly the case in the mechanical alloying process described in the next section.

2.3.6. Mechanical Alloying

Mechanical alloying is strictly speaking another powder metallurgical process, but is only similar to the more common PM route once the blending stage is completed. Mechanical alloying involves high speed attrition of elemental (or pre-alloyed) powders, such that alloying occurs by the continual shearing and cold welding of particles during milling. This is shown schematically in figure 2.5. MMCs are produced in this way by the addition of large (>3μm diameter) SiC particles (≤40vol%) prior to high speed milling.

The extent of alloying can be followed using x-ray diffraction. Mahanty et al [1989]
have shown that 50-75% alloying can be achieved for a 7010 Al-alloy (Al-6.2Zn-2.5Mg-1.7Cu) with 5vol% SiC\(_p\) (14\(\mu\)m) in 12 hours, indicating that processing can be within realistic time limits. Gilman and Sankaran [1988] have found that trace additions do not homogenise well when added as elemental powders and they suggest that these trace elements should be incorporated as prealloyed powders.

### 2.4. Production of Aluminium Alloy Powders

#### 2.4.1. Rapid Solidification

Most aluminium alloy powders for use in the manufacture of MMCs are made by gas atomisation processes, high pressure gas atomisation in particular which is a method of producing powders that undergo rapid solidification (RS) [Jones, 1982]. Engineers tend to define RS by arbitrarily selecting a value of cooling rate that will appear to act as a boundary between the upper limit of "normal" solidification and the onset of "rapid" solidification. Even though RS has been traditionally associated with high cooling rates (>10\(^3\) Ks\(^{-1}\)) it is more appropriate to define it as solidification occurring at high solidification front velocities (>1 ms\(^{-1}\)) which can be the result of high melt undercoolings and/or high cooling rates. As solidification front velocity increases, the scale of the microstructure becomes more refined, i.e. smaller dendrite arm or cell spacing and finer, more evenly distributed precipitates in alloy systems which exhibit the formation of secondary phases. At very high solidification front velocities (>4 ms\(^{-1}\)) solute trapping and extended solid solutions can be attained giving materials which are more chemically homogeneous. This is especially important in aluminium based systems in which no more than a few wt% of many elements can be taken into solution. At the highest solidification rates the nucleation of a crystalline solid can also be suppressed completely and a metastable amorphous structure can form [Jones, 1982].

Metallic glasses are unlikely to appear in the materials in the present study. The refined microstructure is, however, of considerable interest. The main benefits of RS can be summarised as:
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(i) Finer grain size of consolidated material which offers improved tensile properties due to Hall-Petch strengthening, since the grain size is dependent on the prior powder particle size.

(ii) No macrosegregation.

(iii) Much reduced microsegregation due to solidification at high rates and the extension of solid solubility.

(iv) Extended solid solutions increase chemical homogeneity and produce higher volume fractions of finer precipitates in subsequently aged materials, with finer dispersions.

(v) New alloy possibilities due to the extension of solid solubility.

(vi) The formation of amorphous phases.

2.4.2. High Pressure Gas Atomisation

Gas atomisation involves the production of liquid metal droplets by the disintegration of a stream of melt with one or more jets of gas. Atomisation is produced by utilising the kinetic energy of the atomising medium, typically helium, argon, or nitrogen to break up a thin stream of melt. Many atomisation geometries are used in commercial practice. Typically, two or more jets, or an annular ring, are positioned around the axis of the metal stream. The axes of the gas jets are equally inclined to the metal stream axis and intersect this axis at the geometrical impingement point. The facility used in this study is shown schematically in figures 2.6 and 2.7 and has been modified including the design of the die [Ricks et al, 1986], and more recently the provision of a moveable substrate for spray deposition.

Dombrowski and Johns [1986] developed a physical model for the disintegration of thin sheets of liquids (figure 2.8). The impinging gas was considered to initiate a sinusoidal wave in the melt stream which rapidly increases in amplitude. The wave motion then causes ligaments to detach from the bulk liquid. These break down into elongated drops which spherodise to give rounded droplets. More implicit mathematical models of melt stream disintegration are under way [Antipas, 1994].

The overall process of gas atomisation is governed by several interrelated operating
parameters. Controllable variables include jet distance, jet pressure, nozzle geometry, velocity and type of gas, melt flow rate, and melt superheat. In consequence, the interpretation of experimental data is difficult. Several empirical expressions have been proposed that relate particle size distribution to atomisation conditions [Date et al, 1967, Nichiporenko, 1967, Small and Bruce, 1968, Lubanska, 1970, Kim and Marshall, 1971, Lawley, 1977]. Of these, that quoted by Lubanska is the most widely accepted.

It is important to note that it is not possible to produce tailor made powder size distributions by the gas atomisation process because at present the understanding of the break up of melt streams by gas under high pressure is very primitive. The implication is that any PM route processing of MMCs that requires a particular size range will result in a waste of powder. Traditionally, the sieving of matrix powders to obtain a size range has been performed in order to achieve homogeneous dispersions of SiC_p. It would be ideal, until such time as the size distribution of gas atomised powders can be accurately controlled, to produce MMCs with acceptable microstructure and properties without prior sieving and powder separation. This thesis goes someway towards addressing this problem.

Atomisation is often carried out under conditions where a low partial pressure of oxygen is maintained in order for the fresh powder to be oxidised in a controlled manner and allow safe handling in open air [Eddington, 1986]. The resulting oxide films are typically 10-20Å thick [Carney, 1990], and although this has been found to be of little consequence in the Al-Cu binary system, there is evidence to suggest that this may be detrimental to the properties of the consolidated material in more reactive systems.

2.5. Production of Discontinuous SiC Reinforcements

2.5.1. SiC Whiskers
The production of SiC whiskers is through the vapour-liquid-solid (VLS) mechanism
Chapter 2. Metal Matrix Composites

[Evans, 1972]. This involves the nucleation and growth of the whisker from a heterogeneously nucleating liquid droplet (the VLS droplet) which is supersaturated with the elemental components required by the whisker composition. The process for SiC whiskers is shown schematically in figure 2.9. The nucleating VLS droplet in the case of SiC whiskers is liquid steel. The first stage in the VLS process is the diffusion of molecules in the gas phase (SiO, CH₄, H₂) to the VLS droplet. Vapour deposition then occurs at the VLS droplet which is followed by a heterogeneous chemical reaction at the vapour/liquid interface to produce SiC. The SiC then dissolves in the VLS droplet which becomes supersaturated, whilst the reaction by-products diffuse away from it. Si and C then diffuse through the droplet to the liquid/solid interface where they precipitate as SiC and thus causing the whisker to nucleate, lifting the droplet from the substrate. Growth of the whisker then occurs by a continuation of the above deposition and precipitation sequence.

The diameter of the droplet is controlled by the temperature of the system. As the temperature increases the contact angle of the VLS droplet decreases and the spreading occurs which causes the diameter of the liquid/solid interface to increase and therefore the potential diameter of the whisker to increase. The converse also occurs. Thus any fluctuation in the temperature of the system results in whiskers of non uniform diameter. Typical VLS droplets have diameters of 0.1μm implying a similar minimum diameter for whiskers grown by this method. As produced whiskers are between 100μm and 500μm long, but subsequent handling and secondary processing can reduce the length substantially.

2.5.2. SiC Particulates

SiC particulates or powders can be produced either by a sol-gel route from organosilicon gels or from the more usual vapour phase route known as the Acheson process and its derivatives. SiC particulates are available as the α and β polymorphs.

Gels prepared from alkoxy silanes can be used as precursors for the formation of powders capable of pyrolysing to SiC [McColm and Clark, 1988]. Approximately 4.0g
of allyltrimethoxysilane, \( \text{CH}_2=\text{CHCH}_2\text{R(OC}_3\text{H}_3)_3 \), is mixed with 25ml of distilled water and 0.5ml of ethanoic acid, and stirred at room temperature until the solution becomes transparent. Approximately 3ml of concentrated ammonia solution is added and the solution is stirred for sixteen hours. Hydrolysis of the three alkoxy groups and spontaneous condensation polymerisation leads to a cross-linked gel that can then be isolated by decantation and vacuum dried at 353 K (80°C). This acid catalysed route produces powders in the form of hard aggregates, but if a base catalysed route is used then the resulting powders are fine and soft. Pyrolysis at 1173 K (900°C) in argon yields sub-micron SiC powder of the cubic \( \beta \) polymorph.

Large quantities of the hexagonal \( \alpha \) polymorph have been synthesised by the Acheson process [Richerson, 1992]. Figure 2.10 schematically shows the kiln arrangement for the process. The process appears crude, but is cost effective and simultaneously produces lower-grade SiC for abrasives (and reinforcement for MMCs) and high-grade SiC for electrical applications. The Acheson process consists of mixing \( \text{SiO}_2 \) sand with coke in a large elongated mound enclosing a resistance heater. The mound is heated to temperatures in excess of 2473 K (2200°C) at which time the coke reacts with the \( \text{SiO}_2 \) to produce SiC plus CO gas ( \( \text{SiO}_2 + \text{C} \rightarrow \text{SiC} + \text{CO} \) ). Heating is continued until the reaction is completed in the centre of the mound. After cooling, the mound is broken up and sorted. The centre of the mound contains green hexagonal SiC crystals that are low in impurities and suitable for electronic applications. Around the core is a zone of lower purity SiC which is crushed and used for abrasives. The outer layer of the mound is a mixture of SiC product and unreacted \( \text{SiO}_2 \) which is remixed with coke in preparation for the next batch.

SiC can be prepared in this way from almost any source of silicon and carbon. For example, it has been produced in the laboratory from a mixture of silicon powder and sugar. It has also been prepared from rice hulls. SiC prepared from silicon tetrachloride (\( \text{SiCl}_4 \)) and some silanes forms as the \( \beta \) polymorph.

Kinetic studies for the determination of activation energy for the Acheson process have shown the controlling step to be the intermediate vapour phase formation of
silicon monoxide, and that the overall endothermicity of the reactions necessitates a high temperature process. A two stage process has therefore been developed from the Acheson process [McColm and Clark, 1988]. The first stage is to make SiO from silica and silicon. The second stage is to allow the SiO to react with carbon of a desired fine size and morphology. The reaction SiO + C \rightarrow SiC + CO has a slight exothermicity and the overall effect is a lower temperature process. Figure 2.11 outlines this method. Acetylene black is held between carbon felt pads where it reacts with SiO vapour as it passes upward through the charge under the action of a vacuum.

Since the production of SiC particulates based on the Acheson process relies on the crushing of the reaction products, the lower grade of SiC can contain agglomerates of very fine SiC particles. These agglomerates can break on secondary processing of an MMC and therefore local variations in the properties of the MMC may exist.

2.6. Effect of Reinforcement on the Properties of MMCs

2.6.1. Physical Properties
The coefficient of thermal expansion (CTE) of a metal matrix composite (\(a_{\text{comp}}\)) can be described by the rule of mixtures:

\[
a_{\text{comp}} = a_m V_m + a_r V_r
\]

...(2.2)

where the CTE (\(\alpha\)) and volume fraction (\(V\)) of the matrix and reinforcement are denoted by the subscripts \(m\) and \(r\) respectively. Turner [1946] derived an expression for the CTE of composite materials with spherical reinforcements, which includes the thermal conductivity (\(K\)) of the matrix and reinforcement, and assumes only isostatic stress.
A more sophisticated model considering shear as well as isostatic stress has been derived by Kerner [1956]. Measured values of the CTE of 6061/SiC\textsubscript{p} MMCs, shown in figure 2.12, have been found to fall between the values predicted by the latter two models [Walker and Geiger, 1989]. For composites containing non-spherical reinforcements, the thermal expansion is anisotropic when processing introduces a preferred orientation of the reinforcement. Models which predict the expansion behaviour of composites containing oriented fibres, ellipsoids and platelets have also been published [Hale, 1976, Halpin, 1967, Wakashima et al, 1974, Taker and Hatta, 1991].

Geiger and Walker [1991] measured the thermal and electrical conductivities of discontinuously reinforced aluminium based composites. The thermal conductivity of this type of composite, with low volume fractions of approximately spherical reinforcements, has been described by the Rayleigh-Maxwell equation [Rayleigh, 1892]:

\[
K_{\text{comp}} = K_m \frac{1 + 2V \left[ \frac{(1-K_m/K_r)}{(2K_m/K_r+1)} \right]}{1 - V \left[ \frac{(1-K_m/K_r)}{(2K_m/K_r+1)} \right]} \quad ...(2.4)
\]

In general, the thermal conductivity of the reinforcement phase is not well characterised, so composite conductivity cannot be predicted \textit{a priori}. Measurement of composite and matrix conductivity allows \( K_r \) to be calculated, leading to subsequent prediction of thermal conductivity of other composites having the same matrix and reinforcement phases. Thermal conductivities of 2009/SiC\textsubscript{p} and 2009/SiC\textsubscript{w} are shown in figure 2.13. It was found that composites containing SiC whiskers had higher thermal conductivities than those containing SiC particulate for a given volume fraction and matrix. The electrical conductivities of 6061 and 2009 alloys reinforced with SiC\textsubscript{p} are shown in figure 2.14. These data show that a higher electrical conductivity is achieved with the 6061 alloy matrix.
The dependence of the physical properties of MMCs on the volume fraction of the SiC\textsubscript{p} reinforcement has been utilised by Liaw \textit{et al} [1990] for developing non destructive evaluation (NDE) "signatures" of MMCs. The velocity of ultrasound was found to increase linearly with volume fraction of SiC\textsubscript{p} for both longitudinal and shear waves. Eddy current signatures were measured and the readings again increased linearly with volume fraction of SiC\textsubscript{p}. The surface resistivity of the composites was also measured. This too appeared to rise linearly with volume fraction of SiC\textsubscript{p}, but with more scatter. The fit was improved when the total volume fraction of intermetallics and porosity, as well as the reinforcement was taken into account.

\textbf{2.6.2. Recrystallisation and Texture}

The presence of particulate reinforcement in an aluminium alloy matrix has been found to affect the recrystallisation behaviour of the matrix, and the formation of thermomechanically induced textures [Humphreys, 1991].

\textbf{2.6.2.1. Deformation zones}

During cold working the incompatibility between a deforming matrix and a non deformable particle causes the generation of dislocations at the particles. At very low strains (<1\%) these may take the form of unrelaxed dislocation structures such as Orowan loops, but at larger strains such structures relax to form dislocation configurations which depend upon the size and shape of the particle. For particles of the size range encountered in MMCs, the plastic relaxation results in a region close to the particle being rotated with respect to the matrix. This region is known as a deformation zone [Humphreys \textit{et al}, 1990]

Juul Jensen \textit{et al} [1991], and Jiang and Liu [1992] have described the deformation zones for SiC whiskers and particulates of different sizes. Microstructural observations of the deformation zones in cold rolled Al-SiC composites are summarised in table 2.9 [Jiang and Liu, 1992].


**TABLE 2.9. Deformation zones in cold rolled Al-SiC composites**

<table>
<thead>
<tr>
<th>Particle</th>
<th>Zone shape</th>
<th>Zone size*</th>
<th>Subgrain size</th>
<th>Misorientation within zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC&lt;sub&gt;w&lt;/sub&gt;</td>
<td>$d \sim t$</td>
<td>$t = d$</td>
<td>large</td>
<td>large</td>
</tr>
<tr>
<td>SiC&lt;sub&gt;p&lt;/sub&gt; (0.8 µm)</td>
<td>$d \sim t$</td>
<td>$t = 0.5d$</td>
<td>large</td>
<td>small</td>
</tr>
<tr>
<td>SiC&lt;sub&gt;p&lt;/sub&gt; (3 µm)</td>
<td>$d \sim t$</td>
<td>$0.3d &lt; t &lt; 0.5d$</td>
<td>small</td>
<td>large</td>
</tr>
</tbody>
</table>

* $d =$ reinforcement diameter, $t =$ deformation zone size

Whiskers are associated with deformation zones which are not necessarily complete. Large misorientations (>10°) and complete changes of orientation are observed at the whisker ends and in deformation zones of groups of two or more whiskers. For materials with small SiC particles (0.8 µm), deformation zones are observed at the largest particles or groups of particles. The lattice rotations in these zones are small, 2-5°, and only in regions near sharp corners are larger misorientations observed. For composites containing larger SiC particles (3 µm) complete deformation zones develop at particles larger than 2 µm (approximately 95% of the particles). The subgrain sizes in these zones are smaller than those in the deformation zones of materials containing either whiskers or small SiC particles. A high angle boundary is often observed between the deformation zone and the matrix. [Juul Jensen et al, 1991, Jiang and Liu, 1992].

**2.6.2.2. Texture**

Bowen et al [1991], Juul Jensen et al [1991], Jiang and Liu [1992], and Shahani and Clyne [1991] have all studied texture in discontinuously reinforced aluminium based MMCs. In each case a $<111>$ deformation texture was observed after cold deformation, with a weak $<100>$ component. This was the same texture as for the unreinforced material. The presence of a particulate reinforcement, however, weakened this texture due to the lattice rotation in the deformation zones around the
particles. Raising the volume fraction of reinforcement increased the volume fraction of the rotated matrix, which in turn weakened the deformation texture. This has been confirmed by Bowen et al [1991] and Juul Jensen et al [1991]. Bowen et al suggested that the texture is weakened proportionally to the volume fraction of reinforcement up to a loading of 6%, above which the texture remains essentially random. Juul Jensen et al have found that the weakening of the deformation texture is similar for SiC whiskers and large SiC particulate (3μm), but less pronounced for fine SiC particulate (0.8μm). This correlates with the misorientation of the deformation zones of these materials given in table 2.9. For particle sizes greater than 3μm, no substantial effect on the deformation texture is observed [Bowen et al, 1991].

Juul Jensen et al [1991] also observed a weak <012> component in the deformation texture. Although this has not been confirmed in deformation textures, Shahani and Clyne [1991] have found a <320> texture, which is close in orientation to the <012>, in annealed and recrystallised MMCs of a similar type. Bowen et al [1991], Jiang and Liu [1992] and Liu et al [1991] have also found recrystallisation textures between <100> and <110>. This texture again weakens with increasing volume fraction of the reinforcement. This recrystallisation texture has been attributed to the presence of stringers of fine oxide particles pinning the hot worked structure causing nucleation of recrystallised grains in the rotated matrix of the deformation zones of the reinforcement. These oxide stringers are attributed to the incomplete breakup of the Al powder oxide skins during deformation and are actually observed in commercially (air) atomised and consolidated powders.

2.6.2.3. Recrystallisation temperature and grain size
The recrystallisation temperature of deformed PM Al/SiC MMCs has been measured by Humphreys et al [1990], Jiang and Liu [1992], and Juul Jensen et al [1991]. They each found that the recrystallisation temperature decreased with the addition of the reinforcement and the decrease continued with further loading of reinforcement. It was also observed that the recrystallisation temperature reduced with decreasing reinforcement particle size. Humphreys et al explain this by the larger stored energy in the composite materials and by the smaller distance by which grains must grow
before impinging on a neighbouring grain.

Particles of diameter greater than 1\(\mu\)m may stimulate nucleation of recrystallisation in the deformation zones adjacent to the particles. In general at least one nucleus is formed at each particle on annealing, and as a result the grain size will be related to the distribution of particles. The particles used for reinforcement are usually larger than 1\(\mu\)m in diameter, hence there will be extensive particle stimulated nucleation, and the recrystallised grain size of the composite might be expected to be determined by this effect. This indicates that grain size would be controlled by nucleation. The grain size corresponding to one grain per particle, \(D_N\), is given by [Humphreys et al, 1990]

\[
D_N = \frac{d}{V_f^{1/3}} 
\]

where \(d\) is the particle diameter and \(V_f\) is the volume fraction. Computer simulated particle stimulated grain structures have been created by Fridy et al [1992] using an Avrami type equation. The calculated grain size distributions indicate that as the degree of clustering of the reinforcement increases then the width of the grain size distribution also increases. This is in agreement with equation 2.5 above since in a clustered region the local volume fraction will be high resulting in a reduced value of \(D_N\) and conversely in a reinforcement lean region the \(V_f\) will be low and so the resulting value of \(D_N\) will be larger. The calculated grain size distributions of Fridy et al did not however agree well with experimentally measured grain size distributions.

Ceramic particles will pin the grain boundaries and prevent grain growth. When the final grain size is controlled by grain growth and not nucleation, the limiting size to which the grains grow is [Humphreys et al, 1990]

\[
D_g = \frac{2d}{3V_f} 
\]

This indicates that the grain growth limited grain size would be greater than the nucleation limited grain size for low volume fractions.
When the grain size becomes comparable to the interparticle spacing this corresponds to one grain per particle and so $D_G = D_N$. This occurs at around 50vol% of reinforcement. Humphreys et al [1990] have measured the recrystallised grain size for aluminium reinforced with 3μm and 20μm SiC particles of varying volume fraction and compared them with the predicted values for both nucleation controlled and growth controlled grain size. They found that the grain size in the composite containing 3μm particles was controlled by grain growth, whereas that of the composite containing 20μm particles was controlled by nucleation, although the final grain size of the 3μm particle containing material was finer. Considering a whole range of particle sizes, Humphreys et al [1990] have found that the measured grain size, of pure aluminium reinforced with different sized SiC particles at different volume fractions, fits an empirical relationship of the form

$$D = k \frac{d^{3/2}}{V_f}$$  

...(2.7)

where $k$ is a constant.

2.6.3. Fracture

Poor fracture related properties have been identified as one of the major obstacles to the wide use of MMC materials. These properties have been studied for discontinuously reinforced MMCs by a number of research groups. In ductile fracture, which is characterised by void nucleation and growth, the spacing between void nucleating particles is generally considered to be a critical microstructural parameter, and along with the tensile properties controls the toughness of the material. The latter can be represented by the following expression [Firrao and Roberti, 1985]

$$K_{IC} = [a\sigma_y \varepsilon_f^* E f(N)]^{1/2} s^{1/2}$$  

...(2.8)

where $K_{IC}$ is the plane strain fracture toughness, $a$ is a numerical constant, $\sigma_y$ is the yield stress, $\varepsilon_f^*$ is the maximum strain at the crack tip, $E$ is the Young's modulus, $f(N)$
is some function of the strain-hardening exponent and $s$ is the average inclusion spacing in the matrix. A dimpled fracture surface has been the most commonly observed fracture morphology in discontinuously reinforced aluminium [Bayoumi and Suery, 1987, Flom and Arsenault, 1989, Selvaduray et al, 1989, Gauthier, 1990, Birt and Johnson, 1990, Downes and King, 1991, Mummery, 1991, Manoharan and Lewandowski, 1992]. This indicates that the void nucleation and growth mechanism operates for this type of MMC, and that equation 2.8 should be applicable. Geometrically, there is a relationship between $s$, the volume fraction, $V_f$, and the particle size, $d$. One such expression is [LeRoy et al, 1981]

$$s = 0.77dV_f^{-1/2}$$

We can therefore vary $s$ by either changing the reinforcement particle size or its volume fraction.

The fracture toughness of particle reinforced aluminium has been investigated in terms of the crack initiation fracture toughness, $K_{IC}$ [Flom & Arsenault, 1989], and strain energy release rate, $J_{IC}$ [Kim et al, 1992, Manoharan & Lewandowski, 1992]. In each case it was found that the fracture toughness decreased as the volume fraction of reinforcement increased, as a combination of equations 2.8 and 2.9 would suggest.

From equations 2.8 and 2.9 it is obvious that a similar result can be obtained by keeping $V_f$ constant and altering the particle size $d$. This assumes that voids are indeed nucleated by the reinforcing particles and/or the response of the matrix to changes of $s$ remains the same regardless of whether this change is caused by varying the volume fraction or the size of the particles. The effect of SiC particle size on $K_{IC}$ has been investigated by Downes and King [1991] and Arsenault and co-workers, [Flom & Arsenault, 1986, 1989, Arsenault, 1988]. The former have observed that for 20wt% (=18vol%) SiC$_p$ in an 8090 alloy matrix, the composite containing 3µm particles had $K_{IC}=14.0\text{MPa}\sqrt{\text{m}}$. This value fell to 11.5MPa√m for material containing 6µm particles, and rose again with increased particle size up to 12.9MPa√m at a particle size of 23µm. A similar trend was found by the latter workers, who
considered this variation insignificant, since the value of $K_{IC}$ fell to approximately half of its value at the small particle sizes, when their 1100 Al matrix contained 250\,\mu m particles. This led them to the conclusion that reinforcement particle size did not affect the crack initiation fracture toughness until very large particles (>20\,\mu m) were used. However, the $K_{IC}$ parameter behaved in the opposite way to that expected from equations 2.8 and 2.9.

Different trends are observed, when considering the crack growth fracture toughness in terms of the tearing modulus, $T$:

$$ T = \frac{E}{\sigma_y} \frac{dJ}{da} \quad \cdots (2.10) $$

where $dJ/da$ is the rate of change of strain energy release rate with length of crack. Kim et al [1990] have found that the tearing modulus falls from a maximum value at 0vol\% SiC$_p$, slowly at first with increasing volume fraction, then more rapidly to a maximum gradient at about 15vol\%, and then more slowly asymptotically towards $T=0$. This falls in line with the general trend that MMCs become less tough with increasing volume fraction of reinforcement, and hence decreasing interparticle spacing. The tearing modulus has also been found to increase with increasing reinforcement particle size [Flom and Arsenault, 1986, 1989, Arsenault, 1988], approximately linearly up to 20\,\mu m particle size then more slowly up to 250\,\mu m particle size. This increase in crack propagation toughness could be due to an increased ability to accommodate plastic deformation in the matrix with larger interparticle spacing. The main conclusion from this was that whilst crack initiation was little affected by reinforcement particle size, the resistance to crack propagation increased with larger particles.

SiC reinforcement has also been found to have an effect on fatigue crack propagation. Li et al [1992] observed that for aged LY12 Al (similar in composition to 2024 alloy) with 10\,\mu m SiC$_p$, the fatigue crack propagation rate decreased with increasing volume fraction from 6 to 15\%, but only the composite containing 15vol\% SiC$_p$ had a lower propagation rate than that of the monolithic alloy. They suggested
that the decrease in crack propagation rate with increased volume fraction was due
to increased roughness induced crack closure, crack deflection and crack bridging.
Styles et al [1992] have found that the fatigue crack propagation rate in Al-Cu-Mg
alloy MMCs could also be reduced by using a higher temperature solution treatment
to enhance the dissolution of CuAl2 type precipitates which is more sluggish in the
reinforced materials.

2.6.4. Tensile Properties

2.6.4.1. Elastic modulus

The elastic modulus of discontinuously reinforced MMCs is bracketed by two
relationships expressed in terms of the elastic modulus, \( E \), and volume fraction, \( V \), of
the individual constituents. The linear upper bound is defined by the rule of mixtures

\[
E_c = E_m V_m + E_r V_r
\]

...(2.11)

where subscripts \( c \), \( m \), and \( r \) refer to the composite, matrix and reinforcement
respectively. The nonlinear lower bound is defined by a more complicated expression
for materials containing spherical particles, simplified by assuming that the Poisson's
ratio is a universal constant with a value of 0.2 [Hashin and Shtrikman, 1963]:

\[
E_c = E_m \frac{E_m V_m + E_r (V_r + 1)}{E_r V_m + E_m (V_r + 1)}
\]

...(2.12)

The morphology of reinforcement also has a large influence on the magnitude of the
elastic modulus. Figure 2.15 shows the average elastic modulus of a number of
particulate and whisker reinforced aluminium alloys together with the upper and
lower bounds [Walker and Geiger, 1989]. The elastic moduli of the whisker
reinforced materials (loaded in the whisker direction) fall approximately half way
between the predicted limits. The moduli of the particulate reinforced materials also
falls between the predicted limits, but nearer to the lower bound. The monotonic
increase of elastic modulus with volume fraction of reinforcement has also been
observed by Warner et al, [1988], Selvaduray et al [1989], Yang et al [1991],
Bhanuprasad et al [1991], Mummery [1991] and Srivatsan and Auradkar [1991]. No relationship between particle size and elastic modulus has been observed [Mummery, 1991].

2.6.4.2. Strength
The mechanisms and explanations of strengthening in MMCs are numerous and will be discussed separately in section §2.6.6. Only the general trends of the strength of MMCs as a function of the reinforcement volume fraction and particle size will be mentioned here.


Although the particle size of the reinforcement has no effect on the elastic modulus of MMCs, it has been found to affect their yield and ultimate tensile strengths. Geiger and Walker [1991] have demonstrated that the yield and ultimate tensile strengths fall approximately linearly as the square root of the particle size increases. Other workers have also observed the general trend that strength decreases with increasing particle size [Gauthier, 1990, Yang et al, 1990, 1991, Lewandowski et al, 1991, Bhanuprasad et al, 1991]. Mummery [1991] also observed this trend for 1070-Al SiC$_p$ MMCs, but like the effect of particle volume fraction, he did not observe a particle size dependence for the 5050-Al SiC$_p$ MMCs.

2.6.4.3. Ductility
As the volume fraction of reinforcement increases, the elongation to failure of particle reinforced MMCs has been found to decrease [Bayoumi and Suery, 1987, Walker and
Geiger, 1989, Gauthier, 1990, Yang et al, 1990, Bhanuprasad et al, 1991, Geiger and Walker, 1991, Mummery, 1991, Kumai et al, 1992. In compression, Yang et al [1991] have observed the opposite effect up to volume fractions of 30vol% and then a decrease in ductility with greater volume fractions. The ductility of MMCs is also found to decrease as the particle size increases [Bayoumi and Suery, 1987, Yang et al, 1990, Bhanuprasad et al, 1991, Mummery, 1991]. Geiger and Walker [1991] observed that on reducing the particle size from 2μm to 0.7μm there was a severe loss of ductility which was attributed to extensive clustering of the reinforcement.

It can be concluded from these general trends, that unlike toughness, the ductility of particulate reinforced MMCs in tension does not depend upon the interparticle distance of the reinforcement irrespective of the volume fraction and size of the reinforcing particles. As the volume fraction of particulate increases the interparticle space decreases, and so does the toughness and ductility. As the particle size increases, the distance between particles also increases, yet the ductility falls.

2.6.5. Wear

Wang and Rack [1992] have studied the sliding wear of SiC<sub>W</sub> reinforced 2124 alloy in contact with a harder unreinforced steel. They found that as the volume fraction of whiskers increased the wear rate of the MMC decreased exponentially and so the MMC became more abrasion resistant. However, the wear rate of the steel increased indicating that the MMC became more abrasive. They concluded that if clustering of the reinforcement occurred during production, then regions with high volume fractions could initiate cracks and form asperities containing clusters of the reinforcement, and cause increased wear of the contacting surface.

2.6.6. Strengthening Mechanisms

Attempts to interpret and model the strength of particulate reinforced MMCs have ranged from those based on purely continuum analyses and finite element techniques to those based on strict dislocation mechanics. This section describes some of the models and suggested mechanisms for the strengthening of MMCs.
2.6.6.1. Continuum models

The continuum models assume that there is some load redistribution between the two phases, lowering the effective stress in the matrix. Yield is said to occur when the effective matrix stress satisfies a prescribed stress criterion. Inherent in the models is that the matrix is plastically homogeneous and can, therefore, be adequately described by global parameters. However, for the continuum models to work well, the mechanical properties of both the matrix and reinforcement need to be accurately specified, and it is not certain that the bulk properties of these will represent their behaviour in a composite. In general, continuum models can be categorised into three types; load sharing models, finite element modelling, and Eshelby's equivalent inclusion principle.

The most basic load sharing model for particulate reinforced MMCs is that of a modified rule of mixtures [Tomota et al, 1976, Gerbase et al, 1979, Cho and Gurland, 1988]. For an aggregate or alloy consisting of two phases the modified rule of mixtures for stress is given by:

\[ \sigma_c = \sigma_a V_a + \sigma_\beta V_\beta \]  

...(2.13)

where \( V \) is the volume fraction and \( \sigma \) is the average value of the stress in the direction of the applied load, and the subscripts refer to the composite, \( c \), and the two phases, \( \alpha \) and \( \beta \), respectively. The term "modified" is used to indicate that the average values of the stresses in the two phases are in situ values and not the bulk properties as would be the case for the classical rule of mixtures. These in situ values are difficult to determine experimentally.

Another load sharing model is one based on the original shear lag model [Cox, 1952], which has been used to predict the strength of fibre reinforced materials. The tensile transfer of load at the fibre ends was small in comparison to that along the length of the fibre and was therefore ignored. In the case of particles the tensile transfer at the fibre ends cannot be ignored since it makes a significant contribution to load partitioning. Nardone and Prewo [1986] have developed a simplified model based upon this modification to the shear lag analysis. For particulate reinforcements, they
predict the composite yield stress to be given by

\[ \sigma_{cy} = \sigma_{my} \left( \frac{V(S+4)}{4} + (1-V_f) \right) \] ...

where \( \sigma_{my} \) is the matrix yield stress, \( S \) is the aspect ratio of reinforcement, and \( V_f \) is the volume fraction of the reinforcement.

Finite element models have two basic components; a constitutive equation detailing the local material behaviour, and a network or cell structure dividing the entire body. The solutions of the constitutive equations are forced to obey specified boundary conditions at the cell boundaries. An attraction of these models is the prediction of local values of the stress fields. This should enable composite properties governed by these local stresses, such as fracture, to be modelled. The properties of particulate reinforced MMCs have been modelled by finite element techniques with some success [Christman et al, 1989, Levy and Papazian, 1990, Tvergaard, 1990, Dragone and Nix, 1990, Kim et al, 1990]. These models do not, however, predict the observed particle size dependence on yield stress. Additionally, the models are highly sensitive to the form of the constitutive equation and to the cell structure, giving concern over the stability of the predictions.

Eshelby showed that an analytical solution can be obtained for the stress field in and around an elastic inhomogeneity embedded within an infinite matrix under an applied far-field strain, provided the inhomogeneity has an ellipsoidal shape [Eshelby, 1957]. The stress field is disturbed by the presence of the inhomogeneity which is constrained by the surrounding material. By a series of "cutting and welding" exercises, Eshelby showed that the inhomogeneity can be replaced by an equivalent inclusion of the same elastic constants as the surrounding matrix which has undergone a stress-free strain chosen such that it has the same final constrained shape as the inhomogeneity. By calculating the equivalent stress-free strain required to imitate the inhomogeneity, the solution to the inhomogeneous problem is also solved. The stress-free strain, \( \varepsilon' \), and the constrained strain, \( \varepsilon^c \), are linked by Eshelby's accommodation
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tensor, $\Gamma$, which is solely dependent upon the inclusion geometry and Poisson's ratio of the medium

$$ \epsilon^e = \Gamma \epsilon^f $$

...(2.15)

The model has been extended to non-dilute composites containing significant volume fractions of dispersed inclusions by adopting mean field approximations. It is an attractive model as it can be easily extended to model all the elastic properties of the composite, such as modulus and thermal expansion coefficient, as well as the response to an applied stress or strain by a simple superposition of the stresses. The geometrical dependence of $\Gamma$ is primarily a function of the aspect ratio of the particles and not of absolute size, so once again the model does not predict the dependence of yield strength on particle size.

### 2.6.6.2. Dislocation mechanics model

The models based on dislocation micromechanics have had greater success in modelling the properties of low strength matrix composites [Humphreys, 1988, Miller and Humphreys, 1990, 1991]. In these models yield is defined as the onset of dislocation motion through the bulk of the matrix. This occurs when sufficient stress is applied to overcome the barriers to dislocation motion. These barriers are grain and sub-grain boundaries, reinforcement particles, matrix precipitates and solutes, residual stresses, and residual dislocations.

The contribution of grain size, $D$, to the yield stress is given by the Hall Petch equation:

$$ \sigma_{gb} = K_y D^{-\frac{1}{2}} $$

...(2.16)

For Al the constant $K_y$ is typically 0.1MNm$^{-3/2}$ [McElroy and Szkoipiak, 1972] and for fine grained material a higher value of 0.15MNm$^{-3/2}$ has been found [Lloyd, 1980]. If it is assumed that each reinforcing particle of diameter $d$ nucleates a single
spherical grain on recrystallisation then Miller and Humphreys [1990] suggest that the recrystallised grain size, $D$, can be estimated from the particle size, $d$, and volume fraction, $V_f$ by

$$D = d \left( \frac{(1-V_f)}{V_f} \right)^{\frac{1}{3}} \quad \ldots(2.17)$$

The grain sub-structure formed on working the material also has a strengthening effect which has the same form as for grain boundaries, but with the constant $K_y$ taking a lower value.

The large difference in thermal expansion of aluminium (23.5x10^{-6} K^{-1}) and SiC (4.5x10^{-6} K^{-1}) results in the generation of dislocations on cooling from the metal working or solution treatment temperature. The dislocation density may be estimated by assuming that the misfit is relieved by dislocation generation when the mismatch is greater than the Burgers vector, $b$. The misfit is the product of the temperature change ($\Delta T$) and the difference in thermal expansion ($\Delta \alpha$). The simplest geometrical assumption is for all this strain to be relieved by punching of square prismatic loops of side $L$ from the sides of cubic particles. For a linear strain $\epsilon$ across each particle the total length of dislocation generated per particle is $12\epsilon L^2/b$. Since for a particle volume fraction $V_f$ the number of particles per unit volume is $V_f/L^3$ the dislocation density, $\rho$, is given by

$$\rho = 12\epsilon \frac{V_f}{bL} = \frac{12 \Delta T \Delta \alpha V_f}{bL} \quad \ldots(2.18)$$

If it is assumed that the dislocations are uniformly distributed, then the strengthening $\sigma_q$ will be given by an expression such as

$$\sigma_q = \alpha'Gb \sqrt{\rho} \quad \ldots(2.19)$$

where $\alpha'$ is typically between 0.5 and 1, and $G$ is the shear modulus of the matrix.

The elastic stress due to thermal mismatch puts the particles into compression and the matrix into tension. These internal or residual stresses tend to locally surround
each reinforcing particle. In the case of closely spaced particles (i.e. fine particles and/or high volume fractions) these elastic zones interact and are uniformly distributed throughout the material. For fibres or platelets aligned in the direction of testing, the residual stress is anisotropic, resulting in a net residual stress in the direction of alignment. Therefore the yield stress in compression is expected to be higher than the yield stress in tension. For equiaxed particles, the residual stress is essentially isotropic, and the yield strengths are the same in tension and compression.

The Orowan bypassing of particles by dislocations can increase the strength of a material. For equiaxed particles, the increase in yield strength, \( \sigma_o' \), due to the particles is given by

\[
\sigma_o' = \frac{2Gb}{l}
\]

...(2.20)

where \( l \) is the interparticle spacing. Miller and Humphreys [1990] showed that the increase in strength due to Orowan bypassing of reinforcing particles is small. There will be another contribution, \( \sigma_p' \), to the yield strength of the MMC by Orowan passing of matrix precipitates, which is similarly related to the spacing between precipitates, along with precipitate strengthening due to the shearing of coherent precipitates by dislocations. The latter is a complex process which has four components the relative importance of which varies between different alloy systems. These components are an increase in yield stress due to coherency strains; surface hardening due to the resistance of an increase in alloy matrix/precipitate interface caused by shearing; modulus strengthening due to a difference in the shear moduli of the alloy matrix and precipitate; and order strengthening caused by the generation of an antiphase boundary between dislocation pairs.

Having delineated the strengthening contributions, the problem arises as to how to combine them to find a yield stress for the composite. The contributions are not necessarily simply additive because dislocations overcome these stresses and obstacles in different ways. The effect of strong obstacles, such as dislocations and particles,
can be represented by the square root of the sum of the squares of these strengthening effects. The hardening from weak obstacles, such as solutes and internal stresses, can be added linearly. This is acknowledged to be an oversimplification [Humphreys, 1988]. The full description of the yield stress of the composite, \( \sigma_{cy} \), including all of the matrix strengthening terms is

\[
\sigma_{cy} = \sqrt{\left(\sigma_q^2 + \sigma_p^2 + \sigma_o^2 + \sigma_{gb} + \sigma_i + \sigma_s\right)} \quad \text{ ...(2.21)}
\]

where \( \sigma_i \) is strengthening due to the residual stresses, and \( \sigma_s \) is matrix solute strengthening. Since some of these terms are dependent on the absolute size of the reinforcing particles as well as volume fraction of reinforcement, the prediction of the overall yield strength of the MMC now includes the effect of reinforcement particle size, which could not be taken into account by the continuum models. The solute and matrix precipitate strengthening terms are expected to change by the alteration of the ageing behaviour of the MMC.

### 2.7. The Aluminium-Copper System

Phase equilibria in the Al-Cu binary system have been assessed by Murray [1985] and the phase diagram is given in figure 2.16. The Al-rich part of the equilibrium diagram exhibits a eutectic reaction between fcc \( \alpha \)-Al and the equilibrium \( \theta \) phase, \( \text{CuAl}_2 \). Commercial aluminium alloys of the 2xxx series are based on binary Al-Cu alloys containing between two and seven weight percent Cu. The physical metallurgy of such alloys is well documented [e.g. Porter and Easterling, 1987, Reed-Hill, 1973]. These are heat treatable alloys, which undergo precipitation hardening (age hardening). The heat treatment consists of:

(i) Solution treatment in the single phase \( \alpha \)-Al region.
(ii) Rapid quenching to form a supersaturated solid solution of Cu in Al.
(iii) Artificial ageing treatment by heating at an intermediate temperature below the \( \theta \) solvs for the controlled decomposition of the supersaturated solid solution to form finely dispersed precipitates.
The first precipitate to form in the Al-Cu system is not the equilibrium phase, but the metastable coherent Cu-rich GP zones. This is then followed by the precipitation of a series of transition phases with increasing stability. The full precipitation sequence is

\[ \alpha_0 \rightarrow \alpha_1 + \text{GP zones} \rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_4 + \theta \]

where \( \alpha_0 \) is the original supersaturated solid solution, \( \alpha_1 \) is the composition of the matrix in equilibrium with GP zones etc. Although \( \theta \) is the most thermodynamically stable phase, its activation barrier to formation is large due to the high interfacial free energy of its incoherent interfaces. Conversely, the activation barrier for the formation of GP zones is small due to the coherent nature of the precipitate. The activation barriers for the formation of the succeeding phases in turn are also small, as the structures of the precipitates gradually alter to that of equilibrium \( \theta \). The system therefore loses free energy more rapidly through the sequence of metastable phases, than by direct formation of \( \theta \). The metastable solvus curves for GP zones, \( \theta'' \), and \( \theta' \) can be placed on the phase diagram as in figure 2.17 [Murray, 1985]. A series of studies by Nakamura et al [1977, 1980, 1986] have indicated the usefulness of nuclear magnetic resonance as a technique for monitoring the concentration of Cu in the matrix during ageing. This lead to the detection of an extra metastable transition phase, the X-phase, between the \( \theta'' \) and \( \theta' \) stages of the precipitation sequence. The presence of this phase has not been substantiated by any other technique.

### 2.7.1. Description of Phases

#### 2.7.1.1. \( \alpha \)-Al matrix

The \( \alpha \)-Al matrix is a random solid solution of Cu in Al. It has a fcc crystal structure with one atom per lattice point, and lattice parameter of 4.04Å. The crystallographic structure of \( \alpha \)-Al is shown in figure 2.18. The maximum solid solubility of Cu in Al is 5.65wt% (2.40at%) at 821K (548°C) [Murray, 1985] which falls off to less than
0.1wt% (0.04at%) at room temperature.

2.7.1.2. GP zones

Cu rich GP zones were first detected independently by Guinier [1938] and Preston [1938] in the late 1930's, as streaks in X-ray diffraction patterns. It was not until 1958 that they were detected microscopically by Nicholson and Nutting [1958], as strain field contrast in the transmission electron microscope (TEM). Nicholson et al [1958-9] later observed GP zones in other Al alloys.

GP zones originate in the segregation of Cu to single \{100\} planes, forming disc shaped particles one atom thick. The associated displacement of the surrounding matrix extends approximately fifteen layers on each side of the Cu layer. The structure of a GP zone is shown schematically in figure 2.19. Microstructurally, GP zones appear to nucleate homogeneously, however the ability for the formation of GP zones at room temperature would indicate that excess quenched in vacancies also have a role to play.

2.7.1.3. \(\theta''\) phase (GP II zones)

The structure of \(\theta''\) is closely related to that of the GP zones, hence the second nomenclature, GP II zones. It consists of layers of Cu atoms, again on \{100\} matrix planes separated by three layers of Al atoms. This leads to a tetragonal unit cell with \(a=b=4.04\text{Å}\) and \(c=7.68\text{Å}\), and the orientation relationship

\[
(001)_{\theta''} \parallel (001)_{\text{a}}
\]

\[
[100]_{\theta''} \parallel [100]_{\text{a}}
\]

The structure of \(\theta''\) is shown in figure 2.20. \(\theta''\) are larger than the GP zones being up to 10nm thick and 100nm in diameter. The transformation from GP zones to \(\theta''\) occurs by the in situ transformation of the zones which can be considered as very potent nucleation sites for \(\theta''\).
2.7.1.4. $\theta'$ phase

$\theta'$ is also tetragonal with $a=b=4.04\,\text{Å}$ and $c=5.80\,\text{Å}$, with an approximate composition CuAl$_2$. Figure 2.21 shows the crystallographic structure of $\theta'$. The structure again has (001) planes that are identical with $\{001\}_a$. However, the (100) and (010) planes have a different crystal structure to the matrix and a large misfit in the [001] direction. $\theta'$ therefore forms as plates on $\{001\}_a$ with the same orientation relationship as $\theta''$. The broad faces of the plates are initially fully coherent, but lose coherency as the plates grow, while the edges of the plates are either incoherent or have a complex semicoherent structure.

$\theta'$ nucleates on matrix dislocations with two orientations of $\theta'$ plates on any one $a/2<110>$ dislocation. As the $\theta'$ grows, the less stable $\theta''$ dissolves, since the Cu concentration in the matrix close to the $\theta''$ precipitates ($\alpha_2$) is higher than that close to $\theta'$ ($\alpha_3$) causing diffusion of Cu away from $\theta''$ towards $\theta'$.

2.7.1.5. Equilibrium $\theta$ phase

The equilibrium phase also has an approximate composition of CuAl$_2$, but has a more complex tetragonal structure than $\theta'$, with $a=b=6.07\,\text{Å}$ and $c=4.87\,\text{Å}$. There are no matching planes with the matrix and so only incoherent, or at best complex semicoherent, interfaces are possible. The structure of $\theta$ phase is shown in figure 2.22.

$\theta$ nucleates either on grain boundaries or at $\theta'/\text{matrix}$ interfaces. The choice of these nucleation sites is governed by the need to reduce the large interfacial energy contribution to the activation barrier for this phase, caused by the lack of interfacial coherency. The nuclei grow into coarse, blocky precipitates at the expense of $\theta'$. 

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2.7.2. Age Hardening of Aluminium-Copper

2.7.2.1. Unreinforced alloys
The correlation of structural changes with the ageing curves for binary Al-Cu alloys was first studied by Silcock et al. [1953-4] using X-ray diffraction techniques. The ageing curves obtained for alloys with composition 2-4.5wt%Cu, at temperatures of 383K (110°C), 403K (130°C) and 463K (190°C) are reproduced in figures 2.23, 2.24 and 2.25 respectively. The curves show the variation of hardness of the material with ageing time, and the range of time over which each phase exists in the microstructure.

2.7.2.2. Ageing at 383K (110°C)
Immediately after quenching the main resistance to dislocation movement is solid solution hardening, and the material is relatively soft. As GP zones form the hardness increases due to the extra stress required to force dislocations through the coherent precipitates. The misfit perpendicular to the coherent θ' plates, which form next, causes the matrix to be highly strained which further increases the resistance to dislocation movement. With the precipitation of θ' the spacing between the precipitates becomes large enough for the dislocations to begin to bow between them and the hardness begins to decrease. Peak hardness occurs at a specific combination of θ'' and θ'. Beyond this peak the material is said to be overaged.

2.7.2.3. Ageing at 403K (130°C)
The mechanisms of precipitation are the same as at 383K (110°C), however diffusion rates are increased at the higher temperature and the peak hardness is reached considerably earlier. The cost of the heat treatment is therefore reduced greatly. The difference in temperature is not large enough to alter the activation barriers to nucleation significantly. Hence, the size and volume fraction of precipitates are not altered to a level which would change the peak hardness value.

2.7.2.4. Ageing at 463K (190°C)
At 463K (190°C) alloys with less than 3.7wt%Cu are above the GP zone solvus and thus GP zones are completely unstable. The other alloys studied by Silcock et al
[1953-4], 4.0wt%Cu and 4.5wt%Cu are very close to the GP zone solvus and the stability of the zones is hence very low. The first precipitate to form, in either case, is therefore $\theta''$. In this case $\theta''$ precipitates under a smaller driving force than at 403K (130°C) and the resultant precipitate dispersion is coarser. Also, the maximum volume fraction of precipitates is reduced. These two factors contribute to a lower peak hardness, although the increase in diffusion rates, caused by the increase in temperature, aids the speed of the ageing process once again.

### 2.7.2.5. Ageing at room temperature

GP zones can be detected after a few days ageing, although no further change is seen after one year and the precipitation sequence does not proceed further than the GP zone stage.

### 2.7.3. The Effect of Reinforcement on Age Hardening

It has been reported that the inclusion of ceramic reinforcements in Al alloy matrices can affect the ageing process markedly [e.g. Clyne, 1987, Christman and Suresh, 1988, Papazian, 1988, Suresh et al, 1989, Oh et al, 1990, Prangnell and Stobbs, 1991, Schueller and Warner, 1991, House et al, 1991, Kim et al, 1992, Lee et al, 1992, Cottu et al, 1992, Bhagat et al, 1992]. Ageing can be altered by a change in the precipitation sequence, or a change in the speed of nucleation and growth of precipitates. The overall cause in both cases is the incidence of very high dislocation densities around the reinforcing phase. These networks of dislocations are formed during the relaxation of the very high internal stresses caused by the difference in coefficient of thermal expansion (CTE) between the matrix and the reinforcing phase. These internal stresses can often be so large as to cause bending in asymmetrically reinforced composites, or be relaxed by creep at elevated temperatures [Mykura and Mykura, 1992].

#### 2.7.3.1. Generation of dislocations

The appearance of high dislocation densities around reinforcing particles has been observed [e.g. Warner et al, 1988, Arsenault and Wu, 1988, Suresh et al, 1989, Mahon...
et al, 1990, Kim et al, 1990, Oh et al, 1990, Arsenault et al, 1991, Taya et al, 1991, Cottu et al, 1992]. Mahon et al [1990] observed two types of dislocation in quenched SiC₆ reinforced 2124 alloy. One type were helices formed in the matrix slightly away from, and occasionally in contact with, the SiC whiskers. These were formed as a result of condensation of excess vacancies onto pre-existing screw dislocations, and thus must have been formed during the early stages of quenching whilst the vacancies were still mobile. The second type of dislocation were those seen at the ends of the SiC whiskers, which often appeared to terminate in the Al/SiC₆ interface at a corner.

Kim et al [1990] modelled the plastic relaxation of thermal misfit stresses in composites, which incorporated the volume fraction of spherical ceramic particles. They found that the dislocation density dropped off with distance from the reinforcing particle in a similar way to the predicted plastic strain energy. The dislocation density was also affected by the volume fraction and size of the ceramic particles. As the volume fraction was increased, the dislocation density increased, and the dislocation structure became more tangled due to the interaction between thermal misfit stress fields. It was also noted that the dislocation density increased with increasing reinforcement particle size. Arsenault et al [1991], Arsenault [1986] and Flom and Arsenault [1986] however, found the reverse effect with increasing particle size for 1100 Al reinforced with 20vol% SiC₆.

The shape of the reinforcing particle has also been found to have an effect on the dislocation structure. When whiskers are used as the reinforcing phase then plastic relaxation and dislocation generation occur at the ends of the whiskers [Warner et al, 1988, Mahon et al, 1990]. Likewise when particulates are used, high dislocation densities are found at sharp corners of the particulate [Warner et al, 1988]. Finite element modelling of MMCs has substantiated these effects [Christman et al, 1989, Levy and Papazian, 1991]. Many finite element models for particulate reinforced MMCs assume a rigid spherical reinforcement [Zahl and McMeeking, 1991, Bao et al, 1991], which may be inappropriate due to the shape effect on plastic relaxation.

Arsenault and Wu [1988] have found that the dislocation densities surrounding the
reinforcement are the same for liquid route Al/SiC_p and PM route Al/SiC_p, so long as the bonding between reinforcement and matrix is the same, with the same size, distribution and volume fraction of the reinforcement.

2.7.3.2. Precipitation

The dislocation structures formed on quenching have been found to alter the precipitation of phases during the ageing process in Al alloy MMCs. For instance, House et al [1991] and Bhagat et al [1992] have reported that peak Vickers hardness occurs at shorter ageing times for 6061 alloy reinforced with both SiC whiskers and alumina particles when aged at 423K (150°C). Papazian [1988] used differential scanning calorimetry (DSC) to investigate this for 6061 alloy reinforced with 20% SiC_w and found that the β" and β' phases precipitated at an earlier stage.

Oh et al [1990] have studied a number of Al alloy MMCs. They found that peak ageing occurred earlier in the Al-Cu-Li system when reinforced with SiC whiskers, and with the use of DSC, attributed this to the accelerated precipitation of the θ' and T_1 phases. They also found that the Al-Cu-Mg system exhibited accelerated ageing when reinforced with SiC_w and attributed this to preferential nucleation of θ' and S' phases on the high dislocation densities surrounding the SiC_w reinforcement. Their DSC results, and those of Papazian on the same system, exhibited only a very small peak shift and also implied a reduced volume fraction of precipitate in the matrix. Christman and Suresh [1988] also reported accelerated ageing in this system, and used transmission electron microscopy (TEM) to study the variation in size of the S' precipitate with ageing time. They found that not only did the S' nucleate earlier in the reinforced material, but it grew at a faster rate. Dutta and Harper [1992] found in a 2014 alloy reinforced with 10 or 15% Al_2O_3 particulate that the precipitation of θ" and θ' were accelerated, whilst that of the S' precipitate was decelerated. They also observed that the volume fraction of S' formed was reduced with little effect on θ'. Accelerated ageing has also been observed in the Al-Si-Mg [Cottu et al, 1992] and the Al-Li [Miller et al, 1992] systems, whilst no change in DSC traces for the 7475 alloy has been observed [Papazian, 1988].
The ageing characteristics of the Al-Cu binary system has been of much interest too. Suresh et al [1989] have followed the ageing of Al-3.5wt%Cu alloys using measurements of the matrix microhardness, and found that the presence of SiC_p at levels of 6, 13 and 20vol% caused accelerated ageing at 463K (190°C). The reason for this was said to be the preferential nucleation of $\theta'$ at the regions of high dislocation density around the reinforcement. Prangnell and Stobbs [1991] also showed this to be the case in his TEM studies. However, the volume fraction of SiC_p did not appear to have a significant effect.

Lee et al [1992] found no change in the ageing characteristics when Al-3.4wt%Cu was reinforced with 10vol% SiC_p either in terms of microhardness of the matrix or DSC traces, when aged at 433K (160°C). The DSC results of Oh et al [1990] were in agreement and this was attributed to the annealing out of the dislocations at the ageing temperature.

Kim et al [1992] reported that the ageing of Al-4wt%Cu, also at 433K (160°C), was suppressed when SiC_w reinforcement was added. Whereas previously in the case of accelerated ageing the time for nucleation of a phase was the cause, here the cause was a change in the volume fraction of a phase. DSC traces showed similar peaks for the precipitation of $\theta'$, but peaks of reduced intensity for the precipitation of $\theta''$ in the reinforced cases. This indicated that as the volume fraction of reinforcement increased, the volume fraction of $\theta''$ which would precipitate out reduced. This suppression of $\theta''$ precipitation was thought to be caused by a lack of quenched in vacancies following the solution treatment due to the availability of a large number of vacancy sinks at the reinforcement/matrix interfaces, or at the increased number of dislocations around the reinforcing particles.
Figure 2.1. Relative costs of MMCs based on 6061-aluminium alloy with 10vol% of discontinuous reinforcements. [Kjar et al, 1989].
Figure 2.2. Schematic of the infiltration technique. [Mykura, 1991].
Figure 2.3. Schematic of the co-spray deposition process. [Willis, 1988].

Figure 2.4. Schematic of a PM route for the production of MMCs.
Figure 2.5. Schematic of the mechanical alloying process. [German, 1984].

Figure 2.6. The high pressure gas atomiser.
Figure 2.7. The die arrangement of the high pressure gas atomiser. [Norman, 1991]

Figure 2.8. Mechanism of melt stream disintegration during high pressure gas atomisation. [Dombrowski and Johns, 1986].
**Figure 2.9.** Schematic of the production of SiC whiskers by the VLS method.

**Figure 2.10.** Schematic of the furnace arrangement used in the Acheson process for the production of SiC particulates.
Figure 2.11. Schematic showing the furnace arrangement for a low temperature adaptation of the Acheson process. [after McColm and Clark, 1988].

Figure 2.12. The variation of the coefficient of thermal expansion for 6061/SiC<sub>p</sub> MMCs. [Geiger and Walker, 1991].
Figure 2.13. The thermal conductivity of 2009-alloy reinforced with either SiC$_p$ or SiC$_w$. [Geiger and Walker, 1991].

Figure 2.14. The electrical conductivities of 6061 and 2009 alloys reinforced with SiC$_p$. [Geiger and Walker, 1991].
Figure 2.15. The elastic moduli of particulate and whisker reinforced aluminium alloys together with the upper and lower bounds. [Walker and Geiger, 1989].
Figure 2.16. The equilibrium phase diagram for the Al-Cu binary system. [Murray, 1985].

Figure 2.17. The Al rich section of the Al-Cu phase diagram with the solvus lines for the metastable transition phases. [Murray, 1985].
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Figure 2.18. The crystal structure of $\alpha$-Al. [Porter and Easterling, 1987].

Figure 2.19. Schematic of the structure of GP zones in the Al-Cu system. [Gerold, 1954].

Figure 2.20. The crystal structure of metastable $\theta''$. [Porter and Easterling, 1987].
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Figure 2.21. The crystal structure of metastable $\theta'$.
[Porter and Easterling, 1987].

\[
\begin{align*}
&\begin{array}{c}
(001) \text{ Coherent or semicoherent} \\
(100) \\
(010) \text{ not coherent }
\end{array}
\end{align*}
\]

Figure 2.22. The crystal structure of the stable $\theta$ phase.
[Porter and Easterling, 1987].

\[
\begin{align*}
&\begin{array}{c}
\theta
\end{array}
\end{align*}
\]

Incoherent

Figure 2.23. Ageing curves for Al-3-4.5wt%Cu aged at 383 K (110°C).
[Silcock et al, 1953-4].

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Figure 2.24. Ageing curves for Al-2-4.5wt%Cu aged at 403 K (130°C). [Silcock et al, 1953-4].

Figure 2.25. Ageing curves for Al-2-4.5wt%Cu aged at 463 K (190°C). [Silcock et al, 1953-4].
3.1. Mixing Mechanisms

A mixture is defined as "the state formed by a complex of two or more ingredients which do not bear a fixed proportion to one another and which, however commingled, are conceived as retaining a separate existence." [Irving and Saxton, 1967]. Mixing is an operation that is intended to reduce nonuniformity of the mixture. This can only be accomplished by inducing physical motion of the ingredients. Three types of motion can be identified in the mixing process. Brodkey [1966] refers to these as diffusions and classifies them as molecular diffusion, eddy "diffusion", and bulk "diffusion". Molecular diffusion is a process which occurs spontaneously, driven by a chemical potential gradient. It is the dominant mechanism in the mixing of gases, and low viscosity fluids. In turbulent mixing, molecular diffusion is superimposed on the gross random eddy motion, which in turn may occur within larger scale bulk "diffusion" or convective flow process. In solid-solid mixing eddy "diffusion" is rarely reached, molecular diffusion is insignificant, and bulk "diffusion" is the dominant process of mixing.

Bulk "diffusion" involves the movement of fluid particles or clumps of solid from one
spatial location in a system to another. This results in mixing either if the interfacial area between the two components increases, or if the minor component is distributed throughout the major component without necessarily increasing the interfacial area. The former criterion is relevant primarily to liquid-liquid mixing, and the latter to solid-liquid and solid-solid mixing. Mixing by bulk "diffusion" can be achieved by a simple bulk rearrangement of the material, which requires no continuous deformation of the material. This is therefore referred to as bulk-convective mixing or distributive mixing. The repeated rearrangement in distributive mixing can either be random or ordered [Grén, 1967, Hersey, 1975]. The former takes place in V-blenders for instance, whereas the latter forms part of the mixing mechanism in many "motionless" mixers. These two types of distributive mixing are shown schematically in figure 3.1. Mixing by bulk "diffusion" can also be achieved by imposing deformation on a system through laminar flow [Mohr et al, 1957], termed laminar-convective mixing. This occurs in mixers which incorporate stirring blades.

3.2. Characterisation of Mixtures

Tadmor and Gogos [1979] suggest a number of considerations which should be made when characterising the state of a mixture. A complete characterisation would require the specification of the size, shape, orientation, and position of every particle or "cluster size-shape diagrams" to characterise the size and shape of metallic powders by statistical analysis of projected images of the particles. If, however, the minor component was in the form of uniform spheres, then this could be simplified to only the position of the particles within the major component being needed for full characterisation. It is possible that such a complete characterisation is unnecessary for some applications, in which case a simple qualitative measure may suffice, such as colour comparison to a standard. Between these two extremes of complete and qualitative characterisation, remains room for a sound quantitative method for measuring the quality of mixing.
3.3. Gross Uniformity

The first stage in determining the quality of a mixture is to examine the overall or gross uniformity. The term gross uniformity relates to a quantitative measure of the goodness of distribution of the minor component throughout the object or system to be analysed. Tadmor and Gogos [1979] consider the extrusion of blue shopping bags manufactured from rolls of blown film. Bags may be taken from such a roll and examined for colour uniformity. If each bag is found to contain the same amount of blue pigment then there is perfect gross uniformity throughout the film. This would imply, in more general terms, that if only one article is produced from a single blend then perfect gross uniformity would be inherent. The occurrence of perfect gross uniformity does not imply perfect mixing, but does give the assurance of basic uniformity amongst manufactured articles. Alternatively, the analysis in the example might reveal that although each bag may contain the same amount of pigment, individual bags display nonuniformity in the form of patches or streaks of colour. More formally this is known as "texture" or "granularity". Finally, the worst case in the example is that the analysis might reveal varying pigment concentrations among bags, as well as each bag exhibiting its individual texture.

The maximum attainable gross uniformity is controlled by the mixing method, and the actual gross uniformity is determined by the conditions and time of mixing. In random mixing processes the maximum attainable uniformity is given by the binomial distribution [Hodge and Seed, 1977]. Consider a system in which the minor component is uniformly sized particles. The major component can be solid or liquid. In either case, the amount of major component in a drawn sample is considered as a number of particles, each having the same volume as a minor component particle. If the volume fraction of the minor component is $p$ and samples are withdrawn containing a total of $n$ particles, the fraction of samples containing $k$ minor particles is given by
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\[ b(k; n, p) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} \]  \quad \text{...(3.1)}

This shows that the distribution of the minor component in the samples is dependent on both the average concentration of the minor component, \( p \), and on the size of the sample, \( n \). This becomes more evident if the variance of the binomial distribution is considered

\[ \sigma_r^2 = \frac{p(1-p)}{n} \]  \quad \text{...(3.2)}

The more particles the samples contain, the narrower the distribution.

To determine the closeness of a mixture to a random distribution a comparison must be made between the distribution of concentrations of the minor component with that of the binomial distribution. The mean volume fraction of the minor component in \( N \) samples is given by

\[ \bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i \]  \quad \text{...(3.3)}

where \( x_i \) is the volume fraction of the minor component in the \( i \)th withdrawn sample.

The measured distribution can be compared with the expected binomial distribution by use of the statistic, \( \chi^2 \). This testing procedure is very time consuming, and in practice simpler tests are used for evaluating the state of mixing. This is done by calculating "mixing indices" that relate statistical parameters of the samples, variance and mean for example, with the parameters of the binomial distribution. One such index is defined as follows [Lacey, 1954]:

\[ M = \frac{\sigma_0^2 - S^2}{\sigma_0^2 - \sigma_r^2} \]  \quad \text{...(3.4)}

where \( \sigma_r^2 \) is the variance of the random binomial distribution. \( S^2 \) is the variance of the samples:
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\[ S^2 = \frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2 \]  
\text{...(3.5)}

and \( \sigma^2_0 \) is the variance for a completely segregated system, i.e. unmixed:

\[ \sigma^2_0 = p(1-p) \]  
\text{...(3.6)}

It is clear that for this mixing index, \( 0 \leq M \leq 1 \), where \( M = 0 \) for the unmixed state and \( M = 1 \) for the completely randomly mixed state.

An exhaustive list of mixing indices is given by Fan et al [1970], and the relationships between them have been determined by Fan and Wang [1975]. Schofield has suggested that the most rigorous of these mixing indices is that used by Carley-Macauley [1962], and Rumpf and Sommer [1974]:

\[ M = \sqrt{\frac{S^2 - \sigma^2_r}{1 - \frac{1}{N}}} \]  
\text{...(3.7)}

although no clear evidence as to why this should be the case was given.

3.4. Texture

The term texture, in mixtures, has already been introduced as the nonuniformity, observed as patches, or streaks, in mixtures. More generally, texture is a composition nonuniformity which has some unique pattern that can be recognized by visual perception. Thus, a "blind" random sampling of a mixture may reveal compositional nonuniformities, but will reveal little about the character of the texture. Julesz [1975], has studied the visual perception of texture, and refers to two samples with the same concentration of the minor component as having the same first order statistics. Thus, if samples exhibit perfect gross uniformity, then their first order statistics are the same. If two samples have the same first order statistics, but exhibit different textures, then the samples are said to have different second order statistics. An
example of this is shown in figure 3.2. The left and right fields share the same first order statistics, i.e. they have the same number of dots, but there is an apparent difference in their texture. In the latter, the black dots were placed randomly in the field, whereas in the former there is a distance of at least ten dot diameters between the black dots. For measuring second order statistics, Julesz suggests dropping a dipole, a needle for example, on the two textures and observing the frequency with which each end of the dipole land on black dots. Identical frequencies imply identical second order statistics. If a third component was present then third order statistics would have to be taken into account and therefore dipole throwing would have to be replaced by some form of tripod or triangle throwing.

Julesz only considered texture in terms of visual perception, so if a measure of texture is required in practical situations then the concept of texture must be quantified in some way. Two concepts, developed by Danckwerts [1952, 1953] for the characterisation of the state of mixing in chemical reactors, were also suggested for texture characterisation. These were termed the "scale of segregation" and the "intensity of segregation". Consider a geometrically ordered, checkered texture of dark grey and light grey squares, as in figure 3.3. This texture can be characterised fully by measuring the length of the squares (scale of segregation) and the difference in intensity of the dark and light greys (intensity of segregation).

Clearly, a state of perfect textureless compositional uniformity can be obtained by either reducing the scale of segregation to an infinitely small value, or by reducing the intensity of segregation to zero. The quality of a mixture depends on some combination of both the scale of segregation and the intensity of segregation. For instance, figure 3.3 shows that if the scale of segregation is sufficiently small, a large intensity of segregation may be tolerated, and vice versa.

In practice, textures are more complicated than the example given here. The scale of segregation cannot be infinitely small, but has a lower limit dependent upon the "ultimate particle" of the minor component. The ultimate particle is the smallest divisible unit of the minor component i.e. molecules for solutions, or individual
particles for the mixing of powders. Most textures exhibit scales and intensities of segregation which may spread over broad ranges. Nadav and Tadmor [1973] show this with carbon black dispersions in extruded films of low density polyethylene. If the scale and intensity of segregation cannot be expressed as single values then, some means of statistical averaging is needed to render them useful for complex texture characterisation.

3.5. The Scale of Segregation

The scale of segregation is defined, numerically, as the integral of the coefficient of correlation $R(r)$ between concentrations (volume fractions) at two points separated by a distance $r$:

$$ u = \int_0^\zeta R(r) \, dr $$

The integral is taken over values of $r$ between zero and $\zeta$. At $r=0$, both points have the same concentration, therefore the correlation coefficient, $R(0)$, is 1, i.e. a perfect correlation. At $r=\zeta$, there is no correlation between the concentrations at the two points, so $R(\zeta)=0$. The dimension of $u$ is the same as that of $r$. The coefficient of correlation is defined by

$$ R(r) = \frac{1}{Ns^2} \sum_{i=1}^{N} (x_i' - \bar{x})(x_i'' - \bar{x}) $$

where $x_i'$ and $x_i''$ are the concentrations at the points a distance $r$ apart, $\bar{x}$ is the mean concentration, and $N$ is the total number of couples of concentrations measured. The variance $s^2$ is calculated from the concentrations at all points:

$$ s^2 = \frac{1}{2N-1} \sum_{i=1}^{2N} (x_i - \bar{x})^2 $$

The coefficient of correlation varies between 1 and -1, denoting perfect positive correlation (both points in each couple have the same concentration) and perfect negative correlation (one point is pure minor, the other pure major), respectively.
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The plot of $R(r)$ versus $r$ is known as a correlogram. The correlogram from a model mixing experiment [Schofield, 1976] is shown in figure 3.4. Danckwerts [1952, 1953] defined the scale of segregation as the area under the correlogram up to the point at which it first crosses the axis. This definition, however, takes no account of the correlogram beyond the first intersection and hence, no account is taken of the long range mixing. Hall and Godfrey [1965] considered this problem and recommended a technique used by Horwitz and Shelton [1961]. Here the correlogram is compared with that of a standard pattern by a similarity coefficient $Q_{AB}$ defined as

$$Q_{AB} = \frac{\sum r R(r)_A R(r)_B}{\left[\sum R(r)_A^2\right]^{\frac{1}{2}} \left[\sum R(r)_B^2\right]^{\frac{1}{2}}} \quad \ldots(3.11)$$

where the subscripts refer to the two correlograms being compared. Schofield [1970] suggested that the correlogram to be used as the standard should be that for a random mixture with zero scale of segregation, i.e. $R(r)$ is zero for all non-zero values of $r$. This reduces equation 3.11 to

$$Q_{AB} = \frac{1}{\left[\sum R(r)_A^2\right]^{\frac{1}{2}}} \quad \ldots(3.12)$$

3.6. The Intensity of Segregation

The intensity of segregation is defined as [Tadmor & Gogos, 1979]

$$I = \frac{S^2}{\sigma_0^2} \quad \ldots(3.13)$$

This expresses the intensity of segregation as the ratio of the measured variance, $S^2$, to the variance of the completely segregated system, $\sigma_0^2$. When the mixture is
completely segregated \( S^2 = 0 \) and \( I = 1 \). When the concentration is completely uniform \( S^2 = 0 \) and \( I = 0 \). The intensity of segregation lies, therefore, between 0 and 1.

The nature of the intensity of segregation can be better understood by analysing a simple two composition system, as in figure 3.5. Here the intensity of segregation can be calculated theoretically. The volume (or area) fraction of regions of composition \( x_1 \) is \( \phi_1 \), and that of composition \( x_2 \) is \( \phi_2 \) \( (\phi_1 + \phi_2 = 1) \). The average concentration and the variance, assuming that the samples taken for examination are smaller than the size of the regions of different compositions, are

\[
\bar{x} = \phi_1 x_1 + \phi_2 x_2 \tag{3.14}
\]

and

\[
S^2 = \phi_1 (x_1 - \bar{x})^2 + \phi_2 (x_2 - \bar{x})^2 \tag{3.15}.
\]

The intensity of segregation is obtained by substituting equations 3.15 and 3.6 (with \( \phi_1 \) replacing \( p \)) into equation 3.13 to give

\[
I = \frac{\phi_1 \phi_2 (x_1 - x_2)^2}{\phi_1 (1 - \phi_1)} = (x_1 - x_2)^2 \tag{3.16}.
\]

Clearly, the intensity of segregation does not depend upon the relative size of the regions, and only reflects the departure of concentrations from the mean.

3.7. Practical Approaches to Mixture Characterisation

A number of attempts have been made to characterise mixtures without the need to resort to tedious mathematical treatments such as those outlined previously. These methods fall into four categories:

(i) methods based on the packing of particles;
(ii) methods based on chemical or physical properties;
(iii) quantitative microscopy;
(iv) geometrical methods.

3.7.1. Particle Packing

Gurland [1961] defined two terms which introduce the use of the packing state of particles to characterise mixing. The first is the "contact between particles". Here the interfacial area per unit volume and the average fractional area of contact per particle can be measured independently of size, shape and distribution. Further to this the average number of contacts of a particle with neighbouring particles of the same phase can be obtained from uniform spheres. The second of Gurland's terms is that of "continuity". The degree of continuity is defined as the probability of infinitely long chains of particles in contact. This probability can be calculated from the average number of contacts per particle, assuming uniform size and random distributions. Akao et al [1976] have estimated the average contact number for random mixtures of particles and the distribution of contact numbers in the completely mixed state.

Both the approaches taken by Gurland [1961] and Akao et al [1976] assume a random or near random distribution of the minor component, and hence are of no significant aid to the characterisation of highly segregated mixtures. No account is taken of nonuniformity of particle shape or size in either the major or minor components. Any practical application of these methods, could only take place if there is no disturbance of the particulate. Clearly, this would make spot sampling extremely difficult, since any insertion of a probe into the mixture would cause disturbance [Schofield, 1976]. Careful compaction of the mixture and sectioning could improve this. However this could cause contacts to occur which were not present in the original blend, or deformation of soft particulates by a harder second phase component.

3.7.2. Chemical or Physical Properties

The effect of the concentration of a second phase on the mechanical and physical properties of a material have been reviewed extensively by Ondracek [1986, 1987]. The idea of a relationship between the volume fraction of the second phase and the
properties of a material has led to the use of local physical properties as a measure of local concentrations, and hence, of the spatial distribution of the second phase.

Best and Tomfohrde [1959] have characterised carbon black dispersions in polyethylene using microdensitometer measurements of relative transmitted light intensity along linear scans of the material. Typical traces for "good" and "poor" dispersions are shown in figure 3.6. These are then translated into relative light intensity distributions and compared with each other. Since this is a lineal analysis it will only give a measure of the homogeneity of the dispersion in one direction, and so ignores any isotropy in the texture, unless measurements are repeated at a number of angles. The technique also presupposes that there is perfect gross uniformity amongst the compared materials. Whilst this may be a good technique for these particular materials, mixtures with limited changes of translucency with concentration of the minor component cannot be analysed in this way, and therefore this method could not be universally accepted as a technique for the measurement of mixture homogeneity. This could be said for any other technique which relies on a physical property of the material.

Lange and Hirlinger [1985], and Altan et al [1990] have used energy dispersive X-ray analysis to characterise alumina/zirconia and copper/tungsten mixtures respectively. The technique involves taking a number of spectra, at different positions in the sample, at a series of magnifications (i.e. varying area of analysis). The standard deviation of the X-ray concentration of the minor component is plotted as a percentage of the mean against the magnification or area scanned. Results from the alumina/zirconia mixtures are given in figure 3.7. If the analysis is performed over very small areas then there is a large variation in concentration, i.e. if the area analysed is significantly smaller than the size of the minor component particle then only minor particle X-rays or major particle X-rays are detected and the variation is very large. As the area of analysis increases the variation falls until a plateau is reached at which point the analysis area is significantly larger than the scale of segregation. As the scale of segregation increases, the plateau is reached at larger areas of analysis and so the curve is translated. The work by Lange and Hirlinger
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[1985] also shows the effect of volume fraction of the minor component on the position of these curves for well mixed blends, but neither groups of workers have investigated the effect of changing the minor component particle size whilst keeping the volume fraction constant.

Whilst this would seemingly be a very useful technique, there are a number of problems associated with it. Spreading of the electron beam in the material causes subsurface X-rays to be emitted, causing an error in the analysis on the plane of investigation. Lateral spreading of the beam increases the area of analysis by an unknown amount. This is negligible for large analysis areas, becoming increasingly significant as the area of analysis is reduced to the area of the incident beam. Lange and Hirlinger [1985], and Altan et al [1990] specifically chose mixtures in which the two components did not contain the same elements, or in which the peaks of the two X-rays used for the separate components did not overlap. Any mixture which did not conform to these two criteria would be very difficult to characterise.

3.7.3. Quantitative Microscopy

A large number of texts review quantitative microscopical methods for determining particle size distributions and volume fractions of a second phase [e.g. DeHoff and Rhines, 1968, Underwood, 1970, Pickering, 1976]. These techniques have found much use in the measurement of non-metallic inclusions in steels [Kiesling, 1978, Pickering, 1979]. Later texts concentrated on automated quantitative microscopy, image analysis particularly [Exner and Hougardy, 1988]. These texts largely ignored the use of quantitative microscopy or stereology for the characterisation of mixtures or the homogeneity of two phase distributions. It was not until the late 1980s that any serious attempts were made towards this goal, firstly for regular arrays of particles [Waechter and Windelberg, 1986], and then for real dispersions [DeHoff, 1986].

Eisenkolb [1966] assessed mixtures of particulates, and suggested that different methods should be used for the determination of coarse and fine distributions. For coarse distributions of the minor component he recommended the use of the standard deviation of localised concentration normalised by the mean. The composition need
not be measured by quantitative microscopy in this case, but by the method, whether utilising a physical, chemical, or microscopical property, most suitable to the mixture to be analysed. For fine distributions, Eisenkolb recommended statistical methods based on "linear counts", "distribution on areas" or the "smallest particle distance". The "linear count" method involves counting the number of each particle species which lie along lines in the mixture. For each line, the frequency of each species is determined. The absolute value of the difference between the frequencies on each line is summed (or the summation of the squares of the differences). The smaller these sums, the better the values of the two species coincide, and the better the degree of mixing between them. Eisenkolb realised that this would be dependent on the bulk concentration of the minor component and only suggested that this method be used for a 1:1 ratio of minor to major component. This is severely limiting since this ratio, which is by number of particles, is also dependent on the relative particle size and the relative densities of the two components. This method is also very sensitive to the direction in which the counts are measured, hence any anisotropy in the texture may be missed.

"Distribution on areas" involves splitting the microscope field into squares, counting the number of minor component particles in each square, and taking the relative standard deviation of the number of particles in each square as with the coarse distribution measurement. Whilst resolving the directional nature of the previous method somewhat, by adding a second dimension, it does not tell us whether the particles in any one square are uniformly spaced or in clusters, i.e. it does not give any information about the formation of conglomerates of particles within the studied areas.

The "smallest particle distance" method accounts for the presence of clusters to some extent. The distance of each particle from its nearest neighbour, $f_i$, is measured and the total of the squares of these distances is formed:
As the value of $F$ decreases, i.e. particles become closer, the tendency to clustering of the particles increases. Eisenkolb quantified this tendency in terms of a "coefficient of grouping":

$$\alpha = 1 - \frac{F}{F_0} \quad \ldots(3.18)$$

where $F_0$ is the summation of the nearest neighbour distances for a uniform distribution of particles. The value of $\alpha$ indicates the tendency for clustering but does not yield information about the number or size of the clusters, i.e. a large number of small clusters could exhibit the same value of $\alpha$ as a small number of large clusters. Calculation of $\alpha$ depends largely on knowing $F_0$, however the particle size of the major component will act as a constraint upon the distribution of the minor component, and so it may not be possible to obtain a uniform distribution in practice. A mathematical description of $F_0$ would therefore prove useful. A number of expressions exist for the description of mean inter-particle distances [Saxl et al, 1987, Corti et al, 1974], all of which assume particles to be spherical and monosized. All practical mixtures exhibit a distribution of particle sizes, where the shape of the particles are not necessarily spherical, SiC whiskers for example. This will have a marked effect on the interparticle distance.

DeHoff [1986] has characterised the evolution of microstructure during the sintering process of materials produced by a powder metallurgical route. In particular, the devolution of the pore structure was of interest. Stereological methods were used to determine the surface area, volume fraction and curvature of pores in the green state and consolidated materials in various sintered states.

Ondracek and Renz [1989] have used a combination of chemical analysis and quantitative microscopy to evaluate the homogeneity of the phase distribution in multiphase materials. The technique involves firstly obtaining a chemical map by
e

electron probe microanalysis. Quantitative image analysis of the maps is then used to determine the average and standard deviation of the concentration of the components.

Radial distribution functions have been used by Petts [1991] in an attempt to characterise the spatial distribution of points based on the microstructures of nickel silicide precipitates in amorphous silicon and SiC$_p$ reinforced aluminium. This technique is based on the variation of some function of the number of points which lie within an imaginary disc, superimposed on the microstructure, with the radius of the imaginary disc. One such function is the mean number of points per unit area in a disc of radius $r$, divided by the mean number of points per unit area over the whole sample. For a highly clustered distribution this function would be expected to show a pronounced peak before settling towards unity, this peak being absent in the case of a regular distribution. A second function is the probability that a disc of radius $r$, centred on a sample point, contains at least one other point. For a clustered distribution this function approaches unity at lower disc radii than for an unclustered region. Petts only applied these functions to microstructures which did not show a high degree of clustering of the second phase. He also indicated that the shape of the functions are very sensitive to the choice of disc radius interval, and the sample size for each radius value. This implies that the technique has to be applied numerous times with different sampling variables to ensure that the shape of the radial distribution function is in fact representative of the spatial distribution of the second phase and is not obscured by effects of sampling. The usefulness of radial distribution functions is therefore questionable especially in the case of highly complex microstructures.

3.7.4. Geometrical Methods

The characterisation of second phase dispersions by geometrical means was introduced by Wray et al [1983]. This method was the construction of tessellating polygons based on microstructures of real materials. This tessellation procedure is known as the Voronoi or Dirichlet tessellation, or the radical line construction. The
Dirichlet tessellation divides the area of the microstructure into a network of cells. This network is a series of polygons, each of which contains one second phase particle such that all points within a cell are closer to the centre of the enclosed particle than to the centre of any other. The sides of the enclosing polygon are obtained from the set of perpendicular bisectors of the line segments which join the enclosed particle to its neighbouring particles. Through this procedure a unique area is assigned to each second phase particle such that the entire area is covered with no overlapping cells. A schematic of the method of construction is shown in figure 3.8. The spatial distribution of the second phase particles can then be characterised in terms of the Dirichlet tessellation by the size and shape of cells, the number of sides the cells have, or the local area fractions of cells.

Spitzig \textit{et al} [1985] have used the Dirichlet tessellation to study sulphide inclusions and carbides in steels. Their results demonstrate how the spatial distribution of the second phase affects the tessellation. Figure 3.9 shows the cell network for inclusions in a 0.028%S steel. Where the inclusions are wide apart, the Dirichlet cells are large, and vice versa. Clusters of inclusions therefore, appear as regions containing small cells. Figure 3.10 shows the tessellation for a 0.004%S steel which has a more uniform distribution of inclusions and therefore a more uniform distribution of cell sizes. The shape of clusters of particles also alters the appearance of the cell network. If the inclusions appear as stringers then the cells at these regions exhibit an aspect ratio with their long direction perpendicular to the length of the stringer. This is shown in figure 3.11, which is the Dirichlet tessellation for a longitudinal section of the 0.028%S steel.

The Dirichlet tessellation has been applied also to composite materials. Along with work on steels Spitzig \textit{et al} [1985] have produced a single tessellation for an aluminium-graphite fibre composite perpendicular to the fibre length. Brockenbrough \textit{et al} [1992] have produced a tessellation for Si particles in an Al-10wt%Si binary alloy, and have proposed a geometric measure of clustering. This utilizes the local area fraction of the particles in constructing a series of chains of \( n \) neighbouring cells such that the combined local area fraction of the cells in the chain is the largest of...
any possible chain of $n$ cells. This is done for a successively increasing number of cells in the chain, $n=1,2,3,...$. A plot of local area fraction of particles versus area fraction of cells in the chain for each successive chain is then termed the "material signature for particle clustering". Along with finite element analysis, Brockenbrough et al have used this method to show that the highest internal stress and strain fields in the material occur at the highest density of Si particles. This analysis was done for an area which contained only sixty particles. For very high numbers of particles this method would become extremely tedious due to the very large number of computations necessary. The combination of Dirichlet tessellation and finite element analysis has also been used by Davy and Guild [1988] for modelling the elastic properties of composites of spherical filler particles embedded in a matrix. In this case a theoretical random distribution of particles was used and the tessellation described mathematically for the input parameters of the finite element analysis.

A technique akin to the Dirichlet tessellation is the use of image analysis for the construction of "zones of influence" [Adler and Melia, 1994]. These zones can be formed either by serially dilating the images of the individual second phase particles, or by applying a distance transform function to the binary image of the microstructure [Adler and Hancock, 1994]. The distance transform function assigns a value to a pixel of the binary image which is the smallest distance of the pixel from any pixel contained within the second phase. The boundaries of the zones of influence occur at the maxima of the distance transform function. Like the Dirichlet cells, the zones of influence each contain a single particle, but whereas the size and shape of the Dirichlet cells are dependent solely on the positions of the particles, the zones of influence are also dependent on the size and shape of the particles. This leads to the conclusion that the Dirichlet tessellation technique is a better indicator of the characterisation of the spatial distribution of second phase particles.
Figure 3.1. Two types of distributive mixing. (a) random. (b) ordered. [Tadmor and Gogos, 1979].
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Figure 3.2. Schematic showing the concept of first and second order statistics. (a) at least ten dot diameters between dots. (b) random. [Julesz, 1975].

Figure 3.3. Schematic showing the concepts of scale and intensity of segregation. [after Tadmor and Gogos, 1979].
Figure 3.4. The correlogram from a model mixing experiment. (a) diagrammatic representations of samples within five mixtures numbered 0 to 4. (b) the correlograms for each of the patterns in (a). [Schofield, 1976].

Figure 3.5. A simple two component system for the calculation of the intensity of segregation. [Tadmor and Gogos, 1979].
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Figure 3.6. Microdensitometer traces for relative transmitted light intensity measurements along linear scans of polyethylene with carbon black dispersions. (a) good dispersion. (b) poor dispersion. [Best and Tomfohrde, 1959].

Figure 3.7. Plots of the variation of relative concentration of zirconia in alumina/zirconia composites with magnification/area analysed. [Lange and Hirlinger, 1985].
Figure 3.8. The Dirichlet tessellation construction.

Figure 3.9. The Dirichlet network for a 0.028%S steel. [Spitzig et al, 1985].
Figure 3.10. The Dirichlet network for a 0.004%S steel. [Spitzig et al, 1985].
Figure 3.11. The Dirichlet network for a longitudinal section of the 0.028%S steel in figure 3.9. [Spitzig et al, 1985].
PART II

THIS STUDY
4.1. Production of Al-4wt%Cu Powders

Ingots of nominal composition Al-4wt%Cu were prepared by induction melting high purity aluminium and copper. The small cast ingots were remelted in the top chamber of the high pressure gas atomiser under an argon atmosphere. The atomising conditions used for producing the powders are summarised in table 4.1 below. Powders were produced with mass median diameters 80\,\mu m, 64\,\mu m, 50\,\mu m, 40\,\mu m and 35\,\mu m. Oxygen free nitrogen was used as the working fluid for producing the coarser grades of powder (80\,\mu m, 64\,\mu m and 50\,\mu m), and helium for the finer grades (40\,\mu m and 35\,\mu m).
TABLE 4.1. Atomising conditions for Al-4wt%Cu powders.

<table>
<thead>
<tr>
<th>Particle Size (Mass Median)</th>
<th>80μm</th>
<th>64μm</th>
<th>50μm</th>
<th>40μm</th>
<th>35μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomising Gas</td>
<td>Nitrogen</td>
<td>Nitrogen</td>
<td>Nitrogen</td>
<td>Helium</td>
<td>Helium</td>
</tr>
<tr>
<td>Nozzle Diameter (mm)</td>
<td>2.00</td>
<td>2.00</td>
<td>2.15</td>
<td>2.10</td>
<td>1.50</td>
</tr>
<tr>
<td>Charge Mass (kg)</td>
<td>2.49</td>
<td>2.34</td>
<td>2.00</td>
<td>2.35</td>
<td>1.72</td>
</tr>
<tr>
<td>Atomising Gas Pressure (MPa (psi))</td>
<td>2.07 (300)</td>
<td>2.07 (300)</td>
<td>3.45 (500)</td>
<td>3.45 (500)</td>
<td>3.45 (500)</td>
</tr>
<tr>
<td>Melt Temp (K (°C))</td>
<td>1213 (940)</td>
<td>1210 (937)</td>
<td>1301 (1028)</td>
<td>1274 (1001)</td>
<td>1153 (880)</td>
</tr>
<tr>
<td>Over-pressure (kPa (atms))</td>
<td>17.23 (0.17)</td>
<td>17.23 (0.17)</td>
<td>17.23 (0.17)</td>
<td>17.23 (0.17)</td>
<td>14.19 (0.14)</td>
</tr>
<tr>
<td>Duration (secs)</td>
<td>171</td>
<td>168</td>
<td>118</td>
<td>146</td>
<td>170</td>
</tr>
</tbody>
</table>

4.2. Characterisation of Al-4wt%Cu Powders

The atomised Al-4wt%Cu alloy powders were characterised in terms of their size distribution, shape, and microstructure.

The size distributions of powders were measured using a Malvern Mastersizer laser granulometer with a 300mm focal length lens. Powders were suspended in water with a single drop of Nonidet P.45 wetting agent, and ultrasonically agitated to the same level prior to measurement to break up any agglomerates. The pump and stirrer speeds were kept constant at 60% and 50% of the maximum respectively.

The shape of the atomised powders was studied with Cambridge S250 and S100 scanning electron microscopes (SEM). Specimens were prepared by thinly dispersing powder onto double sided sticking tape on a sample stub, tapping off
excess powder, and gold sputter coating to form a continuous conductive film.

The microstructure of the powders was examined using optical (reflected light) microscopy and transmission electron microscopy (TEM). Specimens for optical microscopy were produced by mixing powder with finely ground conductive bakelite in a ratio of 1:2, placing a thin layer of the mixture in the Struers Prontopress, placing a thicker layer of granular bakelite on top, and hot pressing. The specimens were ground and polished using standard metallographic techniques on a Struers Planapol automatic polishing machine. The polishing routine was as follows:

<table>
<thead>
<tr>
<th></th>
<th>Lubricant</th>
<th>Wheel Speed</th>
<th>Load</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>until flat</td>
</tr>
<tr>
<td>1000#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>1min</td>
</tr>
<tr>
<td>4000#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>30sec</td>
</tr>
<tr>
<td>Polishing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3μm Dur cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>1μm Dur cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>Finishing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¼μm Mol cloth</td>
<td>pink</td>
<td>150rpm</td>
<td>by hand</td>
<td></td>
</tr>
</tbody>
</table>

Blue and Pink lubricants are Struers proprietary products

Specimens were etched by swabbing for a few seconds with Keller's Reagent (1% HF, 2.5% HNO₃, 1.5% HCl, in water), and immediately washing in copious amounts of water.

TEM specimens were prepared using a copper plating process as discussed in [Adkins et al, 1991]. This involved copper plating a dispersion of powder adhered to a stainless steel substrate. The plating containing the powder particles was peeled from the substrate and mechanically polished from the side which contained no particles until a thickness of ~150μm was reached. 3mm discs containing a high density of particles were punched out and polished to a good finish on both sides.
Chapter 4. Experimental

The discs were finally ion beam thinned to perforation at an angle of 15 degrees and then at 10 degrees for one hour to extend the thin area.

4.3. Characterisation of SiC_p

The size distributions of nominally graded 3\( \mu \)m, 17\( \mu \)m and 29\( \mu \)m SiC_p were examined using the Malvern Mastersizer.

Specimens of the SiC_p were examined for shape and topography in the Cambridge S250 SEM, prepared similarly to those of alloy powder samples.

4.4. Production of MMCs

Six MMCs were produced (see table 4.2). These were based on 40\( \mu \)m and 50\( \mu \)m Al-4wt%Cu powders each with 3\( \mu \)m and 17\( \mu \)m SiC_p, and 80\( \mu \)m and 35\( \mu \)m matrix powders both with 29\( \mu \)m SiC_p. It should be noted at this point that contrary to other practices the atomised powders were not separated into specified size fractions, but only screened below 200\( \mu \)m to remove the flaked material which is produced before steady state atomisation occurs. The separation of fine aluminium powders is realised to be inherently unsafe, but moreover, introduces a cost penalty, increases the complexity of the overall production, and has dangers for material contamination if equipment is not thoroughly clean and the humidity of the atmosphere is not controlled.
TABLE 4.2. Combinations of matrix and reinforcement powder sizes used for the production of MMCs

<table>
<thead>
<tr>
<th>Matrix Particle Diameter (μm)</th>
<th>Reinforcement Particle Size (μm)</th>
<th>Matrix:Reinforcement Particle Size Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>29</td>
<td>1.21</td>
</tr>
<tr>
<td>40</td>
<td>17</td>
<td>2.35</td>
</tr>
<tr>
<td>80</td>
<td>29</td>
<td>2.76</td>
</tr>
<tr>
<td>50</td>
<td>17</td>
<td>2.94</td>
</tr>
<tr>
<td>40</td>
<td>3</td>
<td>13.33</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
<td>16.67</td>
</tr>
</tbody>
</table>

All MMC production was carried out at the DRA (Aerospace Division), Farnborough. The production route was as follows:

(i) Baking of SiC_p for approximately one hour at 473 K (200°C) to drive off any excess moisture present.

(ii) Weighing (20wt%SiC_p) and blending of particulate mixtures in a Turbula T2C blender for one hour at the medium speed.

(iii) Cold compaction of blended material into aluminium cans (57mm diameter) to a maximum load of 100 kN.

(iv) Vacuum degassing at 803 K (530°C) for several hours to prevent porosity caused by adsorbed species and to break up the thin oxide films present on gas atomised aluminium alloy powder particles.

(v) Hot isostatic pressing (HIPping) for 90 minutes at a temperature of 803 K (530°C) and a pressure of 245 MPa followed by slow cooling.

(vi) Machining off of cans to give cylindrical compacted material (~45mm diameter, 70mm height).

(vii) Hot forging at 748 K (475°C) to a thickness of 33mm, and then to 22mm after a reheat of 20mins. Preheating at 748 K (475°C) was for one hour.

(viii) Hot rolling at 748 K (475°C) to 2mm thickness in fifteen passes, with several minutes reheat between passes. Preheating at 748 K (475°C) was for one hour.

Rolled sheets of monolithic Al-4wt%Cu alloys based upon batches of powder of
35μm and 64μm mass median diameters were also produced following the same production route as the MMCs for use as reference materials.

The optimum blending time of one hour was confirmed by measuring the mass median particle size of samples of blends. This was done using the Malvern Mastersizer laser granulometer. Details of these experiments are given in appendix 1.

### 4.5. Characterisation of HIPped MMCs

The microstructures of the as HIPped materials were characterised by reflected light microscopy and TEM. Specimens for reflected light microscopy were mounted in conductive bakelite, and ground and polished using the Struers Planapol machine. The polishing schedule was as follows:

<table>
<thead>
<tr>
<th>Grinding:</th>
<th>Lubricant</th>
<th>Wheel Speed</th>
<th>Load</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂ paper</td>
<td>water</td>
<td>300rpm</td>
<td>120 N</td>
<td>until flat</td>
</tr>
<tr>
<td>120#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>320#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>500#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>800#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>1200#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>2400#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
<tr>
<td>4000#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>2min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polishing:</th>
<th>Lubricant</th>
<th>Wheel Speed</th>
<th>Load</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>6μm Mol cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>120 N</td>
<td>4min</td>
</tr>
<tr>
<td>3μm Mol cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>90 N</td>
<td>4min</td>
</tr>
<tr>
<td>1μm Mol cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>60 N</td>
<td>4min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Finishing:</th>
<th>Lubricant</th>
<th>Wheel Speed</th>
<th>Load</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPS suspension</td>
<td>water</td>
<td>150rpm</td>
<td>60 N</td>
<td>1min</td>
</tr>
</tbody>
</table>

*OPS is a Struers proprietary product based on an alumina suspension.
Optical microscopy was carried out on a Zeiss Axiophot microscope in normal reflected light, and differential interference contrast (DIC) modes.

Specimens for the TEM were first cut from the bulk material as foils a few hundred micrometres thick. 3mm discs were punched out of these and subsequently ground to approximately 100μm thick. The discs were then dimpled to approximately 30μm thick, and ion beam thinned. Thinning took place at an beam angle of 15 degrees until perforation and then at 10 degrees to enlarge the thin area. Specimens were examined on a Jeol 200CX TEM set at an accelerating voltage of 160KeV.

4.6. Characterisation of Rolled MMCs

The as rolled MMCs were examined by reflected light microscopy. Specimens were mounted in conductive bakelite, and polished using the same procedure as for the HIPped materials. Specimens included sections taken in the three orthogonal axes parallel and perpendicular to the rolling plane, and sections close to the edge of the rolled sheet. The grain structure was revealed by anodising samples in a solution of 2ml HF in 49ml methanol and 49ml water at a voltage of 30V d.c., and viewing with crossed polarising filters. Measurements of grain size were made using the linear intercept method.

4.7. Heat Treatment

Four methods were used to study the ageing process in the MMCs and the reference monolithic materials. The heat treatment was of a T6 designation i.e. solution treatment followed by artificial ageing. The solution treatment was carried out at 803 K (530°C) for one hour followed by a cold water quench. Specimens were immediately replaced into a furnace at 463 K (190°C) for artificial ageing, for different times between 0.5 hours and 500 hours, followed by a cold water quench.
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The aged specimens were then refrigerated to prevent any further ageing which might have taken place at room temperature. The following methods were used to study the ageing process:

(i) Microhardness of the matrix was measured using a 5g load to produce indents small enough to fit between reinforcing particles.

(ii) Vickers bulk hardness was measured using a 20kg load.

(iii) X-ray diffractometry (XRD) was used to study the change in lattice parameter of the matrix as ageing proceeded (Cu $k_\alpha$ radiation, 1° split monochromator).

(iv) Differential Scanning Calorimetry was used to study the precipitation sequence of the matrix. Scans were taken from room temperature to 873K (600°C) at a heating rate of 10 K/min using a Mettler TC 10A thermal analyser with DSC20 attachment. The instrument was previously calibrated with pure indium, lead and zinc for temperature and heat flow. MMC samples were all of the same weight, and samples of the monolithic alloy weighed the same as the matrix portion of the MMC samples. All samples were hermetically sealed in pure aluminium crucibles.

MMC specimens for microhardness and bulk hardness were mounted in Struers Epofix cold setting resin and polished using the same procedure previously used for the MMC materials. Unreinforced specimens were also mounted in Epofix and polished as follows:

<table>
<thead>
<tr>
<th>Grinding</th>
<th>Lubricant</th>
<th>Wheel Speed</th>
<th>Load</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>320#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>until flat</td>
</tr>
<tr>
<td>500#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>1min</td>
</tr>
<tr>
<td>800#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>1min</td>
</tr>
<tr>
<td>1200#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>1min</td>
</tr>
<tr>
<td>4000#SiC paper</td>
<td>water</td>
<td>300rpm</td>
<td>90 N</td>
<td>1min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polishing</th>
<th>Lubricant</th>
<th>Wheel Speed</th>
<th>Load</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>6µm Mol cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>120 N</td>
<td>4min</td>
</tr>
<tr>
<td>3µm Mol cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>90 N</td>
<td>4min</td>
</tr>
<tr>
<td>1µm Mol cloth</td>
<td>blue</td>
<td>150rpm</td>
<td>60 N</td>
<td>4min</td>
</tr>
</tbody>
</table>
4.8. Mechanical Testing

Tensile testing was carried out on all rolled materials, in the as-rolled, the peak aged, and the solution treated and cold water quenched conditions. All testing was carried out using an Instron 1175 static testing machine with a 100kN load cell. Strain measurements were made with an extensometer with a 25mm gauge length. Tests were carried out with a cross-head speed of 1mm/min. Specimens were cut from the rolled strip with polycrystalline diamond tipped milling tools to the dimensions shown in figure 4.1.

Tested specimens were stored carefully to preserve the fracture surfaces for examination. Fractography of the tested specimens was carried out on a Cambridge S250 SEM, the specimens having been gold sputter coated first to prevent charging of any SiC_p that might have been present on the fracture surfaces.

The fractured specimens were also sectioned and polished for optical microscopy to examine the effect of tensile testing on the reinforcement. Specimens were prepared as described above in section §4.5.

To study the effects of the size and spatial distribution of the reinforcement on the fracture properties of the MMCs notched tensile specimens were also produced and tested. The specimens used were of similar dimensions to the unnotched specimens but with 60° notches of 1mm depth cut in the centre of the gauge length at each edge (see figure 4.2). Testing of the notched specimens was carried out under the same conditions as that for the unnotched specimens.
4.9. Spatial Distribution of SiC<sub>p</sub>

Four techniques were used in an attempt to quantify the spatial distribution of the SiC<sub>p</sub> reinforcement in the MMCs produced in the present work. Each technique is an example of the use of either quantitative microscopy, a geometrical method, or a technique based on local chemical analysis for evaluating the homogeneity of two-phase materials.

The variation in local volume fraction of reinforcement measured using a Quantimet 920 image analyser was considered first. Several problems arose during this. At low magnifications the image analyser was unable to resolve the spaces between the reinforcing particles. This was particularly problematic in the MMCs containing 3μm SiC particles. Also at these low magnifications each particle was represented by a small number of pixels and so the calculation of the area of the particles was inaccurate. Again this was especially predominant with the smaller SiC particles. The polished SiC particles exhibited birefringence and hence there was considerable contrast within individual particles. Even with careful thresholding the binary images were affected by this and a large amount of manual processing of the images was required. A great number of analyses were needed to yield usable data and the technique was therefore considered to be too impractical for further use.

The distributions of spacings between SiC particles were measured for each of the MMCs. This was done on polished specimens in a Zeiss Axiophot microscope, under normal bright field illumination, using a calibrated graticule in the eyepiece of the microscope. The spacings were measured along linear intercepts across the material, as in figure 4.3.

Dirichlet tessellations were constructed from reflected light photomicrographs of polished sections of the rolled MMCs. The distribution of Dirichlet cell areas and the area fraction of clustered Dirichlet cells were then obtained from each of the constructions. A computer program was also written to generate random
simulated microstructures and their associated Dirichlet tessellations. The code for this program and comments on its structure are given in appendix 2. The Dirichlet tessellation method was described in section §3.7.4.

Local chemical analysis was also used as a final method of determining homogeneity, based on the method described by Lange and Hirlinger [1985]. The technique involved taking energy dispersive X-ray (EDX) analyses on a Jeol 8600X microprobe with Tracor Northern analysis equipment, at different positions on a sample and at increasing magnifications (diminishing areas of analysis). The proportion of Si X-rays to the sum of Al and Si X-rays was evaluated for each analysis, and the mean and standard deviation calculated at each magnification (area). This technique involved large numbers of analyses and hence the microprobe was programmed to automatically move the stage and take analyses, and also to change the magnification at the required intervals. Control of the microprobe by the Tracor Northern analysis equipment incorporated the use of the "TASK", "Flex", and "Flextran" commands within the Tracor Northern Software. The program schedule used for automated control of the microprobe is shown below, with comments on the command functions.

```
201.1  LOCALEDX
201.5  >DB 1 1440 1560
201.10 >DB 2 1690 1810
201.15 >DB 3 1990 8110
201.20 SETUP POINTS 5.99
201.25 LOAD COLUMN 100.5
201.30 GET COLUMN 1
201.35 >WT
201.40 GET POINT 5
201.45 EDS 0 10 100
201.50 >WT
201.55 >TY(12)
201.60 WHEN KK=30 CHANGE MAG 1000
201.65 WHEN KK=60 CHANGE MAG 3000
201.70 WHEN KK=99 END
201.75 GET POINT
201.80 GOTOTO LOCALEDX,45
201.85 END
```

First must contain program name.

Sets up regions of interest on the EDX spectrum, for Al, Si and Cu.

Prompts user to set up coordinates of each position to be analysed.

Loads data file for column conditions into memory, changes the column conditions from any preset conditions to those in the data file (i.e. those required for this analysis). Line 201.35 suspends the program from running until this is done.

Sends microprobe stage to coordinates for first analysis (N.B. points 1-4 are reserved and cannot be used).

The EDX analysis is performed for X-ray energies between 0 and 10 KeV. The program waits until this is done and then prints out the gross and net number of X-rays detected for each region of interest. The microprobe stage is then sent to the next coordinates for analysis and the program loops back to line 201.45 for the next analysis to be performed. After a predetermined number of analyses have been performed the microscopes magnification is automatically changed (initial magnification is 500x), and
Chapter 4. Experimental

The program ends after the last analysis.

The Tracor Northern system only allows a total of 99 points to be set which is insufficient for the total number of analyses required. The numbers of analysis required for this technique is discussed in section §7.3.2. The program above deals with the analysis for magnifications of 500x, 1000x and 3000x. The program is altered appropriately and rerun for the magnifications of 40x and 100x.

A computer program was also written to analogously simulate this technique by measuring local concentrations of dots in random dispersions or arrays of clusters of dots. The code for this program and comments on its structure are given in appendix 3.
Chapter 4. Experimental

Figure 4.1. Dimensions of the specimens used for unnotched tensile tests.

Figure 4.2. Dimensions of the specimens used for notched tensile tests.
Figure 4.3. Schematic diagram showing the linear intercept method for determining the distribution of interparticle spacings.
Characterisation of the Raw Materials

5.1. Characterisation of Al-4wt%Cu Powders

Powders of five Al-4wt%Cu alloys were produced (see table 4.1). The bulk analyses of these powders are given in table 5.1.

TABLE 5.1. Bulk analysis of Al-4wt%Cu alloy powders.

<table>
<thead>
<tr>
<th>Mass Median Particle Size (μm)</th>
<th>Al (wt%)</th>
<th>Cu (wt%)</th>
<th>Fe (wt%)</th>
<th>Si (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>bal.</td>
<td>4.00</td>
<td>0.044</td>
<td>0.14</td>
</tr>
<tr>
<td>40</td>
<td>bal.</td>
<td>3.90</td>
<td>0.025</td>
<td>0.155</td>
</tr>
<tr>
<td>50</td>
<td>bal.</td>
<td>3.97</td>
<td>0.025</td>
<td>0.20</td>
</tr>
<tr>
<td>64</td>
<td>bal.</td>
<td>3.90</td>
<td>0.060</td>
<td>0.115</td>
</tr>
<tr>
<td>80</td>
<td>bal.</td>
<td>4.07</td>
<td>0.065</td>
<td>0.125</td>
</tr>
</tbody>
</table>
Chapter 5. Characterisation of the Raw Materials

There was very little variation in the Cu content from batch to batch which indicates that the feedstock had been weighed sufficiently accurately, and that no solute was lost during the casting procedure. It can be assumed therefore that the microstructure of the final MMCs would not be affected by a difference in composition of the matrix. Fe and Si are the most common impurities picked up, from crucibles and moulds, during the casting process. In all cases these impurity levels were similar and negligibly small again indicating that there was negligible compositional difference between different batches of powder.

Typical size distributions for the as atomised powders are shown in figure 5.1. All powders exhibited symmetrical, uni-modal size distributions.

SEM examination of the atomised powders showed them to be spherical particles with a distinct surface morphology (figure 5.2). Larger particles had a number of small satellites attached to their surface. Some of the largest particles were found to be of an elongated shape, as shown in figure 5.3.

The spherical nature of the atomised particles occurs because the surface tension of the liquid metal droplets is higher than the gravitational forces which would elongate them. The elongated nature of some of the larger powder particles suggests that the larger droplets have enough mass for the gravitational forces to overcome the surface tension and hence prevent spheroidisation. A second explanation could be that in the larger droplets where solidification is slower the thin oxide layer forms whilst the droplet is still liquid and in its ligamental stage (see figure 2.8 in chapter 2). The oxide layer would act as a hard shell and prevent spheroidisation of the droplet.

Reflected light microscopy of sectioned powder samples revealed a cellular microstructure in all particles (figure 5.4). This was confirmed by TEM examination of the powders (figure 5.5).

Jones [1984] has fitted measurements of cell sizes and secondary dendrite arm spacings to a power law relationship with cooling rate, for a number of rapidly
solidified aluminium alloys, giving the empirical expression:

\[ \lambda = B e^{-n} \]  

...(5.1)

where \( \lambda \) is the cell/dendrite arm spacing, \( \epsilon \) is the cooling rate with \( n \approx 1/3 \) and \( B \approx 50 \mu m (Ks^{-1})^n \). Computer modelling has also been used to estimate the cooling rates in HPGA powders. One such model [Ricks et al, 1986] calculates the cooling rate from the heat transfer coefficient between the droplet and the atomising gas, \( h_i \), by

\[ \epsilon = \frac{6(T_{\text{melt}} - T_{\text{gas}})h_i}{c_{\text{metal}} \cdot d} \]  

...(5.2)

where \( T_{\text{melt}} \) and \( T_{\text{gas}} \) are the temperatures of the liquid metal droplet and the atomising gas respectively, \( c_{\text{metal}} \) is the specific heat capacity of the metal and \( d \) is the droplet diameter. \( h_i \) can be determined from the thermophysical properties of the atomising gas by

\[ h_i = \frac{2Kd}{d} + 0.6 \left( \frac{u}{d} \right)^{\frac{1}{2}} (K^2c)^{\frac{1}{3}} \left( \frac{\rho}{\mu} \right)^{\frac{1}{6}} \]  

...(5.3)

where \( d \) is the diameter of the droplet, \( K \) is the thermal conductivity of the gas, \( u \) is the velocity of the gas, \( c \) is the specific heat capacity of the gas, \( \rho \) is the density of the gas, and \( \mu \) is the viscosity of the gas.

Stone and Tsakiropoulos [1992] estimated the cooling rates of gas atomised Al-4wt%Cu alloys atomised with helium and nitrogen, and, by combining particle size/cell size correlations with equation 5.1, derived power law relationships between powder particle size and cooling rates. The estimated average cooling rates for the aluminium alloy powders produced for this study are given in table 5.2.
TABLE 5.2. Estimated cooling rates for atomised Al-4wt%Cu alloy powders.

<table>
<thead>
<tr>
<th>Particle Size (Mass Median)</th>
<th>Atomising Gas</th>
<th>Estimated Cooling Rate (Ks⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80µm</td>
<td>Nitrogen</td>
<td>1740</td>
</tr>
<tr>
<td>64µm</td>
<td>Nitrogen</td>
<td>2356</td>
</tr>
<tr>
<td>50µm</td>
<td>Nitrogen</td>
<td>3296</td>
</tr>
<tr>
<td>40µm</td>
<td>Helium</td>
<td>7626</td>
</tr>
<tr>
<td>35µm</td>
<td>Helium</td>
<td>8704</td>
</tr>
</tbody>
</table>

TEM examination of the as HIPped MMCs was undertaken to determine whether the rapidly solidified microstructure was stable during the early stages of the thermomechanical processing of the MMCs. Thinning of the HIPped materials for TEM examination was difficult due to the different milling rates of the matrix and reinforcement under the action of an ion beam. It was possible, however, to examine the matrix of the MMCs. The matrix of the HIPped MMCs contained large amounts of the \( \theta' \) precipitate (figures 5.6. & 5.7.). \( \theta' \) precipitate free zones were present at grain boundaries, although large precipitates of the \( \theta \)-phase could be found at the grain boundaries (figure 5.8.). The cellular, precipitate free microstructure of the HPGA alloy powder was not stable at the degassing and HIPping temperature of 803 K (530°C). It might therefore be concluded that the matrix of the MMCs would behave similarly to that of conventionally processed alloys.

5.2. Characterisation of SiCₚ

Size distributions for the nominally graded 3µm, 17µm, and 29µm SiCₚ are given in figure 5.9. In each case the distribution was found to be symmetrical and very narrow. Mass median diameters for the SiCₚ samples were 4.65µm, 24.0µm, and 38.8µm, for the 3µm, 17µm, and 29µm grades respectively. Results of particle size analysis of the three grades of SiCₚ indicated mass median diameters greater than the
expected nominal sizes. This is because different methods of particle size analysis yield different measurements dependent upon the principle upon which the technique is based [German, 1984]. For instance, sieve analysis is dependent upon the various feret diameters through a particle, whereas laser granulometry depends upon the particles projected area. The mass median diameters found by Malvern laser granulometry were between 1.3 and 1.5 times the nominal particle size. B.S.3406 [1963] gives conversion factors to assist in the comparison of particle sizes measured using different techniques. The factor to convert from sieve analysis to projected area measurements is 1.40, and that to convert from measurements based on Stokes law to those based on projected area is 1.50. These are both in the range of factors between the measured SiC\(_p\) sizes and the nominal SiC\(_p\) sizes, indicating that the particle size of the SiC\(_p\) was as expected.

SEM examination of the SiC\(_p\) showed the particles, in each case, to be angular with an aspect ratio approximating unity (figure 5.10.). Some platelike particles could be seen, especially in the coarser grades, and a number of particles exhibited striated surfaces. The presence of platelike reinforcing particles could lead to anisotropy of the properties of the MMCs as they have been found to lie along the rolling direction. It is likely that variations in the quantity of these platelike particles would lead to variations in the strength of the MMCs since the shape of reinforcing particles affects the dislocation density and hence the strength. Agglomerates of fine SiC particles could also be found in the coarser grades of SiC\(_p\) (figure 5.11). These are also a potential problem because their presence in large unknown quantities would also affect the strength of the MMCs.
Figure 5.1. Typical size distributions for HPGA Al-4wt%Cu powders (<200μm). (a) coarse grade, \(d_{50}=80\mu m\). (b) fine grade, \(d_{50}=35\mu m\).

Figure 5.2. SEM secondary electron micrograph of typical HPGA Al-4wt%Cu powder particles.
Chapter 5. Characterisation of the Raw Materials

**Figure 5.3.** SEM secondary electron image of a large elongated HPGA Al-4wt%Cu powder particle.

**Figure 5.4.** Reflected light micrograph showing the cellular microstructure of HPGA Al-4wt%Cu powder particles.
Chapter 5. Characterisation of the Raw Materials

Figure 5.5. Bright field TEM micrograph showing the cellular microstructure of HPGA Al-4wt%Cu powders.

Figure 5.6. Bright field TEM micrograph of $\theta'$ precipitates in the matrix of the HIPped MMCs.
Chapter 5. Characterisation of the Raw Materials

Figure 5.7. Bright field TEM micrograph of \( \theta' \) precipitates. \(<100>\) beam direction.

Figure 5.8. Bright field TEM micrograph of a \( \theta' \) precipitate free zone at a matrix grain boundary, but with the presence of a large \( \theta \) precipitate.
Figure 5.9. Particle size distributions of SiC<sub>p</sub> reinforcements. (a) 3µm, \(d_{50}=4.65\)µm. (b) 17µm, \(d_{50}=24.0\)µm. (c) 29µm, \(d_{50}=38.8\)µm.
Figure 5.10. SEM secondary electron image of the 29μm SiC<sub>p</sub> reinforcement.

Figure 5.11. SEM secondary electron image of an agglomerate of fine SiC particles found in the 29μm SiC<sub>p</sub> reinforcement.
The Origins of Inhomogeneity in the PM Route MMCs

6.1. Microstructure of HIPped and Rolled MMCs

On examination of the as HIPped MMCs it was possible to observe the positions of the alloy particles prior to the HIPping process, and the relative positions of SiC particles between them. This structure is termed a "necklace" structure, and was present in all MMCs. The extent to which the structure was necklaced appeared to be dependent on the size of the reinforcing particles in the MMC. MMCs with the 3\(\mu\)SiC\(_{p}\) were grossly necklaced, whilst those containing the larger grades of reinforcement were less extensively necklaced. This is shown in figure 6.1. In addition to the reinforcing particles, a number of inclusions were found in the matrix of the MMCs. These inclusions are characterised in appendix 4, and are not considered further in this thesis.

Figure 6.2 shows the longitudinal sections of three rolled MMCs, with matrix:SiC particle size ratios of 40:3 (13.33), 50:17 (2.94) and 80:29 (2.75), all at the same magnification (longitudinal, long transverse and short transverse sections are defined in figure 6.3). The microstructure of the MMC with the large particle size ratio is
clearly highly segregated with large reinforcement free regions and areas with high concentrations of SiC. The microstructures of the other two MMCs are much more homogeneous than that with the large particle size ratio, but it is unclear as to which of the two has the better spatial distribution of reinforcement, if either.

It is usual to compare microstructures at the same magnification. However, this is questionable when comparing spatial distributions. If the second phase particles are of a constant size in each material then their mean interparticle spacing will be constant, and comparing them at the same magnification would be appropriate. If, however, the size of the second phase particles varies between the different materials then the mean interparticle spacings in each material also varies, since for a constant volume fraction the mean interparticle spacing increases linearly with second phase particle size [Corti et al, 1974].

Thus it is more appropriate to compare the microstructures at magnifications at which the images of the reinforcing particles are the same size and hence the distance between the images of the particles is constant. The microstructures in figure 6.2 have been normalised in this way in figure 6.4. This enhances the perception of variation in homogeneity between the materials, and it is now evident that although two of the materials have almost the same particle size ratio, it is possible to discern between them.

The microstructures of the rolled MMCs were more homogeneous on the transverse planes. Figure 6.5 shows short transverse sections of MMCs of different matrix:reinforcement particle size ratios. Although these microstructures are more homogeneous than the respective microstructures on the longitudinal plane they show that very thin layers of reinforcement free matrix appear to exist between stringer like layers of reinforcement rich material. It can also be seen from figure 6.5 that platelike reinforcing particles, which were noted in the SEM examination of the reinforcement prior to the production of the MMCs, became aligned with the rolling direction during secondary processing. This may introduce a low level of anisotropy into the mechanical properties of the MMCs, although this will not be investigated
further in this thesis.

The microstructures of the MMCs in the rolled condition are formed by the deformation of their respective microstructures in the HIPped condition. Thus a material which is highly segregated after rolling would have had a highly necklaced structure after HIPping. Figure 6.6 shows the microstructures of the same three MMCs in the HIPped condition. The MMC with the large particle size ratio (which was highly segregated after rolling) shows large scale necklacing of the larger matrix particles by the much smaller SiC particles. Necklacing is much reduced for the materials with lower particle size ratios although it is still possible to identify the prior particle boundaries. The microstructures of the HIPped MMCs are normalised in figure 6.7, in a similar fashion to those of the rolled materials (figure 6.4), and once again the perception of the variation in homogeneity is enhanced.

It would be preferable to examine the positions of particles in the mixed state, prior to any consolidation. The process of sampling powder mixtures would inevitably disturb the packing of the particles [Schofield, 1976]. Likewise, any attempt to prepare unconsolidated mixtures for microscopical examination would lead to a loss of the original distribution of particles. The closest alternative to examining loosely packed powder samples was to characterise materials which had undergone some form of isostatic consolidation, HIPping in this case, which would lead to the best retention of the original spatial distribution. The dependence of the rolled microstructures on the respective HIPped microstructures also makes this approach valid.

If, during the mixing process, the particles of both constituents of a two component mixture are considered as rigid spheres, then the spatial distribution of the minor component will be constrained by the relative sizes of the particles. It has already been shown that this leads to a "necklace" structure in PM route particulate reinforced MMCs. In the following sections, the properties of the packing of rigid spheres are used to develop semi-quantitative explanations for the presence and extent of necklacing.
Chapter 6. The Origins of Inhomogeneity in the PM Route MMCs

6.2. The Conversion of Volume Fraction to Number Fraction

A first consideration in determining the extent of necklacing is the proportion of the minor component in terms of the number fraction of particles as a function of volume fraction and, more importantly, the major:minor particle size ratio. The number fraction of minor component, $N_f$, is

$$N_f = \frac{N_{\text{min}}}{N_{\text{min}} + N_{\text{maj}}} \quad \ldots(6.1)$$

where $N_{\text{min}}$ is the number of minor component particles, and $N_{\text{maj}}$ is the number of major component particles. Assuming that the particles in each component are mono-sized, $N_{\text{min}}$ can be described by

$$N_{\text{min}} = \frac{V_{\text{min}}}{P_{\text{min}}} \quad \ldots(6.2)$$

where $V_{\text{min}}$ is the total volume of the minor component, and $P_{\text{min}}$ is the volume of a minor component particle. Similarly,

$$N_{\text{maj}} = \frac{V_{\text{maj}}}{P_{\text{maj}}} \quad \ldots(6.3)$$

where $V_{\text{maj}}$ is the total volume of the major component, and $P_{\text{maj}}$ is the volume of a major component particle. Combining equations 6.1 to 6.3 we get

$$N_f = \frac{\left(\frac{V_{\text{min}}}{P_{\text{min}}}\right)}{\left(\frac{V_{\text{min}}}{P_{\text{min}}} + \frac{V_{\text{maj}}}{P_{\text{maj}}}\right)} = \frac{V_{\text{min}}P_{\text{maj}}}{P_{\text{min}}(P_{\text{maj}}V_{\text{min}} + P_{\text{min}}V_{\text{maj}})} \quad \ldots(6.4)$$

The volume of the minor component, $V_{\text{min}}$, is the volume fraction of minor component, $F$, multiplied by the total volume of the composite, $V_{\text{total}}$. Similarly, the volume of the major component, $V_{\text{maj}}$, is the total volume, $V_{\text{total}}$, multiplied by $(1-F)$. Thus equation 6.4 becomes
Chapter 6. The Origins of Inhomogeneity in the PM Route MMCs

\[
N_f = \frac{FV_{\text{total}} P_{\text{maj}}}{P_{\text{maj}} FV_{\text{total}} + P_{\text{min}} (1-F)V_{\text{total}}} \quad \text{(6.5)}
\]

and this reduces to

\[
N_f = \frac{1}{1 + \left(\frac{1}{F} - 1\right) \frac{P_{\text{min}}}{P_{\text{maj}}}} \quad \text{(6.6)}
\]

For spherical particles

\[
P_{\text{min}} = \frac{4}{3} \pi r_{\text{min}}^3 = \frac{\pi}{6} d_{\text{min}}^3 \quad \text{(6.7)}
\]

and

\[
P_{\text{maj}} = \frac{4}{3} \pi r_{\text{maj}}^3 = \frac{\pi}{6} d_{\text{maj}}^3 \quad \text{(6.8)}
\]

where \( r_{\text{min}} \) and \( d_{\text{min}} \) are the radius and diameter of the minor component particles respectively, and \( r_{\text{maj}} \) and \( d_{\text{maj}} \) are the radius and diameter of the major component particles. Substitution of equations 6.7 and 6.8 in equation 6.6 gives

\[
N_f = \frac{1}{1 + \left(\frac{1}{F} - 1\right) \left(\frac{d_{\text{min}}}{d_{\text{maj}}}\right)^3} \quad \text{(6.9)}
\]

This indicates that the number fraction of the minor component particles in a two component system is a function of the volume fraction of minor component and the particle size ratio of the two components. For a constant major:minor particle size ratio, the number fraction of minor particles increases with increasing volume fraction as would be expected. For a constant volume fraction, the number fraction of minor particles increases with increasing major:minor particle size ratio \((d_{\text{maj}}/d_{\text{min}})\). A plot
of number fraction of minor particles against major:minor particle size ratio, for several volume fractions including that equivalent to the volume fraction of reinforcement in the present work (18.6vol%), is given in figure 6.8. Points are also plotted for the matrix:reinforcement particle size ratios for the materials produced so far for this study. These results are also given in table 6.1.

**TABLE 6.1.** Number fractions of SiC particles estimated from equation 6.9.

<table>
<thead>
<tr>
<th>Al-4wt%Cu Alloy Particle Size (µm)</th>
<th>SiC Reinforcement Particle Size (µm)</th>
<th>Alloy:SiC Particle Size Ratio</th>
<th>Number Fraction of SiC Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>3</td>
<td>13.33</td>
<td>0.9982</td>
</tr>
<tr>
<td>40</td>
<td>17</td>
<td>2.35</td>
<td>0.7478</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
<td>16.67</td>
<td>0.9991</td>
</tr>
<tr>
<td>50</td>
<td>17</td>
<td>2.94</td>
<td>0.8531</td>
</tr>
<tr>
<td>80</td>
<td>29</td>
<td>2.76</td>
<td>0.8277</td>
</tr>
<tr>
<td>35</td>
<td>29</td>
<td>1.21</td>
<td>0.2866</td>
</tr>
</tbody>
</table>

From the materials of this study, those reinforced with 3µm SiC<sub>p</sub> have particle size ratios which lead to estimates of the number fraction of SiC particles extremely close to 1. For the materials with matrix:reinforcement particle size ratios between 2.35 and 3 (which exhibit reasonable homogeneity) the estimated number fraction of SiC particles is between approximately 0.75 and 0.85. The very high number fractions achieved by using the 3µm reinforcement suggest that for a small number of large matrix powder particles there will be very large numbers of small particles between them. Therefore this would lead to a highly necklaced microstructure in materials with these large particle size ratios. The remaining materials with lower number fractions of SiC particles would have less necklaced structures. To achieve, with the 3µm SiC<sub>p</sub>, a number fraction of reinforcement which is similar to the materials with matrix:reinforcement particle size ratios between 2.35 and 3, and therefore a similar
structure, a composite would have to be produced from matrix powder between 7μm and 9μm, which is at the extremes of the current capability of powder production methods. The small reduction in particle size ratio from 2.35 to 1.21 results in a large reduction in the number fraction of SiC particles. This indicates that this approach is sensitive to very small variations in the level of microstructural homogeneity when the microstructures of the MMCs are close to ideal.

A second feature of the family of curves in figure 6.8 is the sensitivity of the number fraction of minor particles to particle size ratio with a change in volume fraction. As the volume fraction of minor particles increases the curve rises towards unity at a higher rate and thus becomes more sensitive to the particle size ratio. In practice this means that if a higher volume fraction of reinforcement is required then there is a lower limit to the matrix:reinforcement size ratio which can be tolerated, and hence for a constant reinforcement size there is a lower limit of matrix powder particle size which can be tolerated. Finer matrix powders are more expensive to produce either due to the costs of using helium instead of nitrogen as the atomising gas, or because of extra wastage of powder after separation of the fine powders by sieving or gas classification.

In the real situation the particles are neither perfectly spherical nor monosized. The SiC particles are angular, but have an aspect ratio close to one, and even the matrix particles are not perfectly spherical (e.g. see figure 5.3 in chapter 5). This would make the calculation of the particle volumes more difficult. The assumption that each component is monosized greatly simplifies the estimation of number fraction. Considering the particle size distributions would introduce two probability density functions into the derivation which would increase the complexity of the calculation greatly. Whilst the scenario described here is an idealised one, it does go some way towards explaining the presence of necklace structures in terms of the numbers of particles of each component.
6.3. The Packing of Particles

It is also possible to consider the presence of minor component clusters in terms of some form of idealised packing of particles. This can be done by considering regular packings of the major phase and then calculating the sizes and possible volume fractions of minor particles which can fill the interstices of the major particles without disturbing the packing of the major particles. Table 6.2 below, gives some of the spatial properties of some simple regular packings of spheres [Cumberland & Crawford, 1987].

**TABLE 6.2. Spatial properties of simple packings of spheres**

<table>
<thead>
<tr>
<th>Packing</th>
<th>Unit Cell Volume</th>
<th>Fractional Solids</th>
<th>Critical Ratio of Entrance</th>
<th>Critical Ratio of Occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive Cubic</td>
<td>$8R^3$</td>
<td>0.5236</td>
<td>2.414</td>
<td>1.366</td>
</tr>
<tr>
<td>FCC</td>
<td>$4\sqrt{2}R^3$</td>
<td>0.7405</td>
<td>6.464</td>
<td>2.415</td>
</tr>
<tr>
<td>CPH</td>
<td>$4\sqrt{2}R^3$</td>
<td>0.7405</td>
<td>6.464</td>
<td>4.44</td>
</tr>
</tbody>
</table>

*R is the sphere radius

The "critical ratio of entrance" is the major:minor component sphere diameter ratio at which a smaller minor component sphere can just pass through the pore formed by the contacting major component spheres in the most densely packed plane. This is shown schematically in figure 6.9. This gives an indication of the largest "small" (minor component) sphere which can fit on this plane. The interstice formed by the large spheres in three dimensions is larger than that in the most densely packed plane. We can therefore define a "critical ratio of occupation" which is the major:minor component sphere diameter ratio at which a small minor component sphere can exist in the three dimensional interstice. It is possible for spheres to fit into this space although they are too large to pass through the interstice on the
densest packed plane, and so for a packing of this type to exist, it must occur during assembly rather than occur as a result of some post assembly "diffusion".

Using this data it is possible to create a map of possible regular structures for various combinations of volume fraction of small spheres and size ratio of spheres (large:small). This map is shown in figure 6.10 for the primitive cubic, FCC, and CPH packings. The left hand boundary of each region is the minimum size ratio of spheres which can be used to fit a small sphere between large spheres in three dimensions, i.e. the critical ratio of occupation. There is no right hand boundary since as the size ratio of spheres increases the small sphere diminishes in size in comparison to the large spheres and so it is always possible to fit a small sphere into the interstice. For each region an upper limit of volume fraction can be defined such that all interstices are filled with the largest possible small sphere. The volume fraction, $F$, is calculated from

$$F = \frac{\frac{4}{3} \pi r^3}{\frac{4}{3} \pi r^3 + AR^3B}$$

...(6.10)

where $r$ and $R$ are the radii of the small and large spheres respectively, $A$ is a structure dependent constant for calculating unit cell volume, and $B$ is the fraction of the unit cell which is solid. The upper limit of volume fraction occurs when $R/r$ is equal to the critical ratio of occupation, i.e. for the primitive cubic case

$$F_{\text{Limit}} = \frac{\frac{4}{3} \pi r^3}{\frac{4}{3} \pi r^3 + (8(1.366r)^3 \times 0.5236)} = 0.282$$

...(6.11)

A cluster can be said to occur when two small spheres can fit in the void between large spheres, and so the onset of clustering occurs when the size ratio of large to small spheres is twice that of the critical ratio of occupation. This therefore splits each region on the map into two at a size ratio of spheres above which clustering is said to have occurred, and below which no clustering occurs. At a size ratio of one
particles of the two components can substitute for each other, and there is no limit on volume fraction.

The position of the real materials in this map should now be considered. The volume fraction of reinforcement in all of the MMCs is 0.186. This is above the volume fraction limits of both the FCC and CPH packings, and only a primitive cubic packing could possibly be attained. The materials containing 3\(\mu\)m SiC\(_p\) have size ratios of 13.33 and 16.67 for matrix powder sizes of 40\(\mu\)m and 50\(\mu\)m respectively, and fall well into the region indicating clustering. This agrees well with the number fraction approach of estimating the presence of necklace structures. Those materials containing 17\(\mu\)m (40\(\mu\)m and 50\(\mu\)m matrix powder) and 29\(\mu\)m (80\(\mu\)m matrix powder) SiC\(_p\) all fall close to the onset of clustering, with the MMC produced from 80\(\mu\)m alloy powder with 29\(\mu\)m SiC\(_p\) falling on the transition between ideal and clustered structures. The proximity of these three MMCs to the transition indicate that a more ideal arrangement of the two component powders could be achieved, although a completely unclustered structure is unlikely. The map also indicates that if 3\(\mu\)m reinforcement is a preferred size then in order to achieve an unclustered structure a matrix powder size of approximately 8\(\mu\)m would be required. This value is in excellent agreement with that estimated using the approach based on the number fraction (see section §6.2).

The MMC with a matrix:reinforcement particle size ratio of 1.21 (35\(\mu\)m matrix powder reinforced with 29\(\mu\)m SiC\(_p\)) lies just to the left of the region of the map which refers to an unclustered primitive cubic pattern. This indicates that if the reinforcement is to be located in the interstitials of primitively packed matrix particles then the matrix particles can no longer touch. However, since the matrix: reinforcement particle size ratio is very close to unity then it is likely that the reinforcing particles will substitute matrix particles rather than pack interstitially.

The above approach to the explanation of the origins of the microstructural inhomogeneity observed in the MMCs of this study assumes that all of the particles are spherical, and that all of the particles of each component are monosized. The
HPGA matrix particles are spherical in nature, and the SiC reinforcing particles have an aspect ratio of close to unity. It is therefore reasonable to assume that all particles are spherical. If the reinforcing particles were elongated then the potential of a particle to fit in an interstice would be controlled by its length.

In the real case, both the matrix powder and the reinforcement exhibit distributions of particle size rather than each species being monosized. If the size distribution of the reinforcement was extremely wide then the approach of idealised packings could not be used. In that case an interstice between major component particles could be filled with either one large minor component particle or many small minor component particles, and a microstructure could therefore exhibit both ideal packing and necklacing at once. The size distributions of the reinforcements of the MMCs in this study were sufficiently narrow for the assumption of monosized particles to be reasonable.

6.4. Attachment of Reinforcement to Matrix Particles

SEM examination of pre-consolidated blended powder mixtures suggests that necklacing of matrix by SiC\textsubscript{p} occurs by the physical attachment of the smaller reinforcement particles to powder particles. The harder SiC particles cause indentations in the softer matrix particles, as shown in figure 6.11. In figure 6.11 the impinging SiC particle has fallen away from the indent, but it is more normal for the reinforcement to become embedded in the surface of the matrix particles, and therefore form a coating of reinforcement around the matrix particles and hence a necklace structure (figure 6.12).

It could be inferred from this that if a sufficiently high energy blending process were used then the SiC particles could become completely enveloped by the matrix due to initial embedding of the SiC\textsubscript{p} and then deformation of the alloy particles during blending. In other words, the matrix particles could no longer be considered as rigid spheres, a homogeneous spatial distribution of the reinforcement could be attained,
and the above two approaches for predicting the microstructure would no longer be valid.

6.5. Concluding Remarks

The microstructures of the rolled MMCs were formed by the deformation of their respective microstructures after HIPping. The HIPped MMCs exhibited a necklaced microstructure of prior matrix particles decorated by SiC particles. The extent to which the structure was necklaced was increased with increasing matrix:reinforcement particle size ratio. The rolled MMCs showed some level of segregation of the SiC\(_p\) reinforcement on the longitudinal plane. The extent of this segregation also increased with increasing matrix:reinforcement particle size ratio. The microstructures on the transverse planes of the rolled sheets were more homogeneous than those on the longitudinal plane although the reinforcement appeared to be in layers with very thin matrix layers between.

The extent of necklacing in the microstructures of the HIPped MMCs, and hence the origins of the microstructures of the MMCs after rolling, have been described in terms of the conversion of the volume fraction of reinforcement to the number fraction of reinforcing particles, and in terms of the ideal packing of rigid spheres. Both approaches suggest that a reasonable level of microstructural homogeneity can be achieved if a matrix:reinforcement particle size ratio of 2.75 or below is employed. This implies that if a reinforcement particle size of 3\(\mu\)m is required then a matrix particle size of below 8.25\(\mu\)m should be used. A more ideal microstructure is achieved when the matrix:reinforcement particle size ratio is much closer still to unity.

The necklacing seen in the as HIPped microstructures also has a small contribution from the attachment and partial embedding of the reinforcement into the softer matrix particles during the blending stage of the manufacturing process.
Figure 6.1. Reflected light micrographs of HIPped MMCs. (a) 3μm SiC\textsubscript{p}. (b) 17μm SiC\textsubscript{p}. 
Figure 6.2. Reflected light micrographs of as rolled MMCs at the same magnification. (a) 40μm matrix powder with 3μm SiC$_p$. (b) 50μm matrix powder with 17μm SiC$_p$. (c) 80μm matrix powder with 29μm SiC$_p$. 
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Figure 6.3. Schematic representation of a rolled sheet indicating the definitions of longitudinal, long transverse and short transverse planes used in this thesis.
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Figure 6.4. Normalised reflected light micrographs of as rolled MMCs. (a) 40µm matrix powder with 3µm SiC\(_p\). (b) 50µm matrix powder with 17µm SiC\(_p\). (c) 80µm matrix powder with 29µm SiC\(_p\).
Figure 6.5. Reflected light micrographs of short transverse sections of two as rolled MMCs. (a) 3 μm SiC	extsubscript{p}. (b) 17 μm SiC	extsubscript{p}.
Figure 6.6. Reflected light micrographs of HIPped MMCs. (a) 40\textmu m matrix powder with 3\textmu m SiC<sub>p</sub>. (b) 50\textmu m matrix powder with 17\textmu m SiC<sub>p</sub>. (c) 80\textmu m matrix powder with 29\textmu m SiC<sub>p</sub>. 
Figure 6.7. Normalised reflected light micrographs of HIPped MMCs. (a) 40μm matrix powder with 3μm SiC<sub>p</sub>. (b) 50μm matrix powder with 17μm SiC<sub>p</sub>. (c) 80μm matrix powder with 29μm SiC<sub>p</sub>. 
Figure 6.8. Plot of number fraction of minor particles against the major:minor particle size ratio for several volume fractions. The MMCs of this study are represented by ×.

\[ \text{RATIO } \frac{d_{c}}{p_{s}} = \frac{1}{\sqrt{2} - 1} = 2.414 \]

(a) Loosest packing

\[ \text{RATIO } \frac{d_{c}}{p_{t}} = \frac{1}{2/\sqrt{3} - 1} = 6.464 \]

(b) Tightest packing

Figure 6.9. Schematic showing the "critical ratio of entrance". [Cumberland and Crawford, 1987].
Figure 6.10. Map showing regions in which it is possible to attain ideal packings with combinations of volume fraction of minor particles and major:minor particle size ratios.
Figure 6.11. SEM secondary electron micrograph of an indented matrix particle after blending with SiC$_p$ reinforcement.

Figure 6.12. SEM secondary electron micrograph of 3$\mu$m SiC$_p$ reinforcement attached to matrix particles after blending.
7.1. Interparticle Spacings

The first method considered for the characterisation of the interparticle spacings of SiC particles in the MMCs was to determine distributions of the number of nearest neighbours and nearest neighbour distances of particles in MMC microstructures, as shown schematically in figure 7.1. Particles which were enclosed in SiC\(_p\) rich regions would have a small number of very close nearest neighbours; particles in SiC\(_p\) lean regions would have a large number of distant nearest neighbours; and those particles which located on the edges of SiC\(_p\) rich regions would have both a very small number of very close nearest neighbours and a large number of very distant nearest neighbours. It soon became evident that this method was impractical, since a large number of measurements would have to be made from a single particle to yield a single "count" for that particle.

A more practical method was thought to be that of measuring interparticle distances along a linear intercept across the microstructure, as shown schematically in figure 4.3.
Figure 7.2 shows the histograms of the distribution of linear intercept interparticle spacings for longitudinal sections (longitudinal, long transverse and short transverse sections were defined in figure 6.3) of two MMCs produced from 50μm matrix powder with (a)3μm (particle size ratio of 16.67) and (b)17μm SiC_p (particle size ratio of 2.94). The linear intercepts were perpendicular to the rolling direction. The distribution for the material containing 3μm SiC_p shows a tall narrow peak at small interparticle spacings with a long tail up to larger interparticle spacings. Although the frequency of very large interparticle spacings is low these spacings are of great significance since they represent a large proportion of the total line length measured and indicate the extent of the presence of SiC_p lean areas. This shows that the material contains a large number of reinforcing particles which are close together, separated by large regions which contain no reinforcement. The distribution for the MMC containing 17μm SiC_p shows a lower, wider peak at the smaller end of the interparticle spacing scale also with a tail up to larger values of interparticle spacing. The range of this distribution is wider than that of the material containing the 3μm reinforcement. This would suggest that the MMC with 17μm SiC_p is less homogeneous than that containing 3μm SiC_p, which is clearly not the case (see figures 6.2 & 6.4). This anomaly arises because for a constant volume fraction of second phase particles the interparticle spacing rises linearly with particle diameter [Corti et al, 1974]. Thus the distribution of interparticle spacings could not be easily compared for MMCs containing reinforcing particles of different sizes.

Normalisation of the distributions is thus necessary. This is done by converting each value of interparticle spacing to its value in terms of number of standard deviations from the mean, \( \bar{x} \), i.e. if a particular value of interparticle spacing was \( x \), then

\[
\frac{x - \bar{x}}{\sigma} = \frac{x - \bar{x}}{\sigma}
\]  

...(7.1)

where \( \bar{x} \) is the mean interparticle spacing, and \( \sigma \) is the standard deviation of interparticle spacings. When figure 7.2 is replotted in this way (see figure 7.3) the range of these normalised plots is the range of the original data in terms of the number of standard deviations. It can now be seen that the range of interparticle
spacings for the MMC with the particle size ratio of 16.67 is approximately nine standard deviations, whereas that for the material with the particle size ratio of 2.94 is approximately six standard deviations. This now shows that the width of the distribution of interparticle spacings is narrower for the MMC with the smaller matrix:reinforcement particle size ratio, as expected from the microscopical examination.

The results of this lineal analysis for longitudinal sections of all of the MMCs are given in figure 7.4, where the range of the normalised interparticle spacing distribution is plotted as a function of matrix:reinforcement particle size ratio. The results show an approximately linear relationship and suggest that in order to achieve a narrow distribution of interparticle spacings, and hence a homogeneous dispersion of reinforcement, the matrix:reinforcement particle size ratio should be as close to unity as possible.

To test the sensitivity of the technique to small variations in dispersion of the reinforcement the above procedure was repeated for linear intercepts on short transverse sections (as defined in figure 6.3) of the MMCs with matrix:reinforcement particle size ratios of 1.21, 2.94 and 13.33. In the first instance this was done in the through thickness direction. Histograms of the normalised interparticle distances for the three MMCs are shown in figure 7.5. The range of the normalised interparticle spacing distribution for the MMC with a particle size ratio of 13.33 was approximately seven standard deviations, which is similar to that of the interparticle spacing distribution on the longitudinal plane. This is an unexpected result since in the MMCs with large particle size ratios the microstructure is significantly more homogeneous in the short transverse plane than in the longitudinal plane, and hence the range of the interparticle spacing distribution should be narrower. This is an indication that the technique lacks sufficient sensitivity at these small variations in scale of segregation. The MMCs with particle size ratios of 1.21 and 2.94 also yield normalised interparticle spacing distributions which are similar in width to those of the same materials in the longitudinal plane. In this case, however, it would be expected that there should be little difference in the width of the distributions on the
Chapter 7. The Spatial Distribution of the Reinforcement

Two planes for both of these materials since there is no obvious large scale difference in the level of homogeneity of the reinforcement on the two planes.

A limitation of a single linear intercept method is that it only yields information along one direction of the material (e.g. perpendicular to the rolling direction on longitudinal sections), and thus ignores any anisotropy in the microstructure. The spatial distribution of the reinforcement could be described more fully if the process is repeated in the rolling direction, and preferably at other angles between the two. This would require at least double the number of measurements and would therefore significantly reduce the practical application of the technique.

The distributions of interparticle spacings for the short transverse sections in the direction parallel to the width of the rolled sheets were also determined. These distributions are shown in figure 7.6. The distribution is very much wider for the MMC with a large particle size ratio, as expected from the microstructural examination, see figure 6.5. The distributions were only slightly wider for the MMCs with particle size ratios much closer to unity, which is also expected. Whereas one would expect the width of the distribution for the MMC with a particle size ratio of 1.21 to be narrower than that with a particle size ratio of 2.94, the opposite was seen. This again highlights that although on large scale microstructural differences the technique is useful there is a lack of sensitivity at small variations in the dispersion of the reinforcement.

7.2. Dirichlet Tessellations

Dirichlet tessellations of longitudinal sections of three MMCs are shown in figure 7.7. For optimum use of the technique constructions should be made from photomicrographs of regions of the specimen which are of small enough magnification such that any other region would appear to be similar, i.e. exhibits gross uniformity. In the case of MMCs of large matrix:reinforcement particle size ratio this was not possible, so constructions were made in typical SiC<sub>p</sub> rich and SiC<sub>p</sub> lean regions (figure
The extent of clustering was first measured. A cluster is said to be formed between two particles if the Dirichlet cell boundary intersects one of the two particles it lies between. In the present study the extent of clustering is defined as the area fraction of Dirichlet cells which contain clustered particles. For the MMCs of large particle size ratios this can be calculated using a rule of mixtures type expression based on the area fractions of clustered cells of the regions that were rich and lean in reinforcement. Thus

\[ C_{\text{ave}} = A_{\text{rich}}C_{\text{rich}} + A_{\text{lean}}C_{\text{lean}} \]  

...(7.2)

where \(C_{\text{rich}}, C_{\text{lean}}\) and \(C_{\text{ave}}\) are the area fractions of clustered cells in SiC\(_p\) rich regions, SiC\(_p\) lean regions and in the composite as a whole, and \(A_{\text{rich}}\) and \(A_{\text{lean}}\) are the area fraction of SiC\(_p\) rich regions and SiC\(_p\) lean regions (\(A_{\text{lean}} = 1 - A_{\text{rich}}\)). For the MMC with a particle size ratio of 13.33 \(A_{\text{rich}}\) was estimated to be 0.25. A plot of the area fraction of clustered Dirichlet cells, \(C_{\text{ave}}\), against the matrix:reinforcement particle size ratio of the MMCs is given in figure 7.8. This plot also contains a point corresponding to the area fraction of clustered regions in the randomly generated microstructure (figure 7.9) which is assumed to have a particle size ratio of unity, although it may be argued that this ratio should be much closer to zero. In reality particle size ratios much less than unity are impractical. The choice of the particle size ratio of the random dispersion does not affect the overall trend that as the matrix:reinforcement particle size ratio falls (i.e. the microstructure becomes more homogeneous) the average area fraction of clustered regions tends towards that of the randomly generated microstructure. It could be envisaged that this method of measuring the extent of clustering would break down if all of the particles were of a uniform size since the intersection of a Dirichlet cell boundary could only occur if two differently sized particles are close together. This is however a highly idealised situation because the probability of two perfectly spherical particles of the exact same size being sectioned similarly is extremely small.
The distributions of individual Dirichlet cell areas were also measured. Similarly to the distribution of interparticle spacings, a homogeneous microstructure would yield a considerably narrower distribution of cell sizes than a microstructure which is highly segregated. However, histograms of the frequency of individual cell areas would be confusing since the average cell area is a function of the average interparticle spacing which, as discussed above, is a function of the particle size of the reinforcement for a given volume fraction of the latter. Cell areas were therefore normalised by the square of the reinforcement particle size. The distributions for MMCs with particle size ratios of 2.35, 2.76 and 13.33 are shown in figure 7.10. Once again the distribution of Dirichlet cell areas for the MMC with the large particle size ratio is calculated from the distributions of SiC_p rich and SiC_p lean regions, and A_{rich}=0.25. The range of the distribution is very much larger for this MMC than for those with particle size ratios closer to unity. However, the distribution is wider for the MMC with a particle size ratio of 2.35 than that of 2.76, whereas from the microscopical examination we would expect the opposite. This indicates that the Dirichlet tessellation technique, like the interparticle spacing technique, lacks sufficient sensitivity to characterise two phase materials with only small differences in level of homogeneity.

The Dirichlet tessellations for short transverse sections of MMCs with particle size ratios of 1.21, 2.94 and 13.33 are given in figure 7.11. Their associated normalised Dirichlet cell area distributions are shown in figure 7.12. These are all narrower than the distributions for MMCs of similar particle size ratios sectioned longitudinally. Again, the width of the distribution does not correlate well with the matrix:reinforcement particle size ratio, and hence the level of microstructural homogeneity, thus confirming the limited sensitivity of the technique.

In order to investigate the use of Dirichlet tessellations for the characterisation of isotropy in the dispersion of second phases, the average linear intercept cell sizes were measured at various angles for the random distribution in figure 7.9, and for two drawn regular arrays of points. Figure 7.13 shows the Dirichlet tessellation for (a) a square array of points and (b) a rectangular array of points with an aspect ratio of
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3:1. These results are plotted (figure 7.14) in terms of cell size relative to the longest dimension of the cell rather than simply cell size since the random distribution and regular distributions were generated by different methods and were therefore not to scale.

Results for the random distribution show little variation of cell size with angle of measurement. Hence the cells have no overall aspect ratio and there is no directionality in the positions of the particles.

For the regular square array of points the cell size is largest at 45° to the side of a cell i.e. across the diagonal of the cell. The variation in cell size is symmetrical about 45° since the cells are square in shape. Other than at 45°, the cells are longest along their edge i.e. at 0° and 90°, and the cell size falls at a decreasing rate until close to the diagonal at 45°.

For the 3x1 rectangular array of points, the Dirichlet cells are rectangles also of aspect ratio 3:1. The largest cell size also occurs through the diagonal of the cell, but this time the variation in cell size is not symmetrical about the diagonal since the Dirichlet cells themselves are not related by mirror symmetry about the diagonal. Hence, other than the anomaly at the diagonal, the cell size falls from the long side of the rectangle (0°) to the short side (90°). It would be expected therefore that as the aspect ratio of the cells increased the rate at which the cell size would fall with angle would also increase, and that the difference in cell length between the longest and shortest sides, at 0° and 90° respectively, would also increase.

The microstructures of all the MMCS are anisotropic to some extent, on both the longitudinal and transverse planes. This anisotropy is on a scale which is much larger than the individual Dirichlet cells which have an aspect ratio of very close to one. Therefore the analysis described above for the characterisation of microstructural isotropy does not hold for the MMCs of this study. It is felt that only microstructures which show very narrow stringers of a second phase with large primary phase regions between could be characterised in this way.
7.3. Local Energy Dispersive X-Ray Analysis

7.3.1. Computer Simulation

A computer program was written for the purpose of illustrating the principle of the EDX technique for the characterisation of the spatial distribution of reinforcement. A flow sheet of the simulation is given in figure 7.15. The simulation begins by generating either a random distribution of dots (single pixels) (figure 7.16), or arrays of square or rectangular clusters of dots where the dots are randomly placed within the clusters (figure 7.17). The overall density of dots, the size of clusters, and the cluster aspect ratio can all be varied. A square measuring box is then randomly superimposed on the generated dispersion, and the number of dots which fall within this box are counted. The box placement is necessarily random since the analysis would be controlled by the geometry of the cluster arrays if the measuring boxes were symmetrically placed. The measuring box is always square, even when the clusters have different aspect ratios, so that direct comparisons can be made between the results of the analysis for random dispersions, square clusters, and rectangular clusters. This is then repeated for a required number of times. The mean, $\bar{x}$, and standard deviation, $\sigma$, of the number of dots counted is then calculated, and from them the coefficient of variation, $\sigma/\bar{x}$, is derived. The box size is then altered and the process repeated. The coefficient of variation is then plotted against the size of the measuring box. This simulation has been used for a number of random distributions of varying dot density, and for a number of arrays of square and rectangular clusters of dots, with constant overall dot density.

Results of the simulation for random dispersions of 2.5%, 5% and 10% dot densities, are shown in figure 7.18. The three curves are of a similar shape. At small measuring box sizes there is a large variation in the number of dots counted in each measurement. The variation quickly falls off towards a plateau close to zero coefficient of variation at larger box sizes. The curves fall towards the plateau at rates dependent upon the overall dot density of the computer generated dispersion, i.e. as the dot density is increased the plateau is reached at smaller box sizes and hence the curve is translated to the left. These results indicate that a generalised
technique for the comparison of microstructures must in some way take into account differences in bulk volume fraction of the second phase.

Figure 7.19 shows the simulated results for different size square clusters (10x10 pixels, 20x20 pixels) for an overall dot density of 5%, along with those for the random dispersion of the same dot density. The curves for the clusters are of a similar shape to that of the random dispersion, but are no longer smooth. They exhibit a damped cyclic type shape, such that minima are reached at a period of twice the side length of the measuring box. This cyclic behaviour is a function of the geometry of the chosen generated structure, and more specifically of the variation in the range of dot counts possible with changing the measuring box size.

Consider the generated microstructure containing clusters of 10x10 pixels. At a measuring box size of 20x20 pixels the range of likely dot counts is very small since at this size the measuring box would always cover the equivalent area of one cluster. When the range is very small, then the likely standard deviation would also be small, and so would be the coefficient of variation. At a measuring box size of 30x30 pixels, however, the range is from a minimum of 20 dots, in which case only one cluster would be covered by the measuring box, to a maximum of 80 dots in which case the measuring box would cover four clusters. This increased range would also increase the likely standard deviation, and thus the coefficient of variation. At a measuring box size of 40x40 pixels the equivalent area of four clusters would always be covered and the range of dot counts would fall again, and consequently the coefficient of variation would also fall. Despite this geometric effect of the chosen cluster arrays there is the underlying dependence of the coefficient of variation of dot counts on the measuring box size as seen in the case of random dispersions and as outlined above. As the simulated microstructure moves from a random dispersion to small clusters and then to larger clusters, that is to say the microstructure becomes less homogeneous, then the curves translate to the right and a larger measuring box is required to distinguish the scale of segregation.

A similar damped cyclic effect is also seen when considering the aspect ratio of
clusters (figure 7.20). Again the period of the cycle is a function of the length of the cluster. As the aspect ratio of the cluster increases the inhomogeneity of the dispersion of dots increases and the curves once more translate to the right.

7.3.2. EDX Analysis

Results of the EDX analyses of longitudinal sections of the MMC materials are given in figure 7.21. The number of analyses taken at each magnification / area of analysis are given in table 7.1. These were the minimum number of analyses required to give reproducible results in the most inhomogeneous material, and hence the results for all the other materials are also reproducible.

**TABLE 7.1. The number of EDX measurements taken at each magnification.**

<table>
<thead>
<tr>
<th>Magnification</th>
<th>Area of Analysis (μm²)</th>
<th>Number of Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>40x</td>
<td>2250x3000 (6.75x10⁶)</td>
<td>12</td>
</tr>
<tr>
<td>100x</td>
<td>900x1200 (1.08x10⁹)</td>
<td>12</td>
</tr>
<tr>
<td>500x</td>
<td>180x240 (4.32x10⁴)</td>
<td>25</td>
</tr>
<tr>
<td>1000x</td>
<td>90x120 (1.08x10⁴)</td>
<td>30</td>
</tr>
<tr>
<td>3000x</td>
<td>30x40 (1.2x10³)</td>
<td>40</td>
</tr>
</tbody>
</table>

The results show curves of similar shape to those of the simulation. There appears however to be no relationship between the point at which the curves deviate from the plateau region and the matrix:reinforcement particle size ratio which has already been shown to determine the level of microstructural homogeneity. A question then arises as to whether it is correct to compare measurements taken at the same area of analysis for materials which contain different sizes of reinforcement, since, as previously stated, for a constant volume fraction the spacing between particles increases linearly with the size of the particles [Corti et al, 1974]. This means that random homogeneous dispersions of particles will only look similar and the resulting analysis will only be similar if the magnification at which we look at them, or the area
we use for analysis, is normalised in some way by the size of the particles. The plot in figure 7.21 is therefore replotted in figure 7.22 where the area of analysis is normalised by the square of the reinforcement particle size. This now shows a relationship between the matrix:reinforcement particle size ratio and the position of the analysis curve, such that as the matrix:reinforcement particle size ratio reduces from large values towards unity, the level of inhomogeneity decreases, and the curve shifts to the left as it is reflected by the computer simulation.

It is possible for the EDX based technique to discern between small differences in the spatial distribution of the reinforcement. This is shown in figure 7.22 by the translation in the analysis curves of MMCs with matrix:reinforcement particle size ratios which are close together, and is a distinct advantage of the EDX based technique over the techniques based on the distribution of interparticle spacing and Dirichlet tessellation discussed in sections §7.1 and §7.2 respectively. To test this further the short transverse sections of MMCs were analysed. The spatial distribution of the SiC\textsubscript{p} reinforcement is inherently more homogeneous on this section, as shown in figure 6.5. The results were normalised by the square of the reinforcement particle size and are shown in figure 7.23. All of these curves are shifted to the left of those determined from the longitudinal sections. The curve corresponding to the material with the large matrix:reinforcement particle size ratio has shifted most of all. This is expected since there is a stronger microstructural difference between the longitudinal and short transverse sections of this material than those with particle size ratios closer to unity. Although the curves corresponding to the more homogeneous microstructures of the short transverse plane are close together there is still a relationship between the level of homogeneity and the point at which the curves deviate from the plateau region.

Even though the EDX based technique is very sensitive to small variations in the level of microstructural inhomogeneity, there are a number of limitations to its use as a universal method for such characterisation. Lateral spreading of the electron beam increases the area of analysis by an unknown amount. This is negligible for large areas of analysis, but becomes increasingly significant as the area of analysis is
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reduced towards the area of the incident beam although this does not in effect occur until long after the analysis curve has deviated from the plateau region. However, even more important are the limitations due to the chemical composition of the two distinct phases, and the positions of the X-ray energy peaks on the EDX spectrum. Lange and Hirlinger [1985] and Altan et al [1990] specifically chose mixtures in which each of the two components contained an element which was not present in the other, and avoided overlapping of the X-ray peaks. The present Al-4wt%Cu/SiC\textsubscript{p} system fulfils these criteria. A SiC\textsubscript{p} reinforced Al-Si alloy, for instance, would be more difficult to characterise since Si appears in both components. Peak deconvolution algorithms could be used to separate overlapping peaks.

7.4. Concluding Remarks

Three practical techniques for the characterisation of the dispersion of second phases have been discussed. The first relies upon determination of the range of the distribution of interparticle spacings on linear intercepts of the microstructure. The second is based upon the range of cell sizes measured from the Dirichlet tessellation constructed from the MMC microstructures. The third technique measures the variation in local chemical composition by EDX analysis.

The former two techniques are based on dimensional measurements taken directly from the microstructure. Both techniques were applied successfully to the PM route SiC\textsubscript{p} reinforced Al-4wt%Cu alloys for large scale differences in dispersion of the reinforcement, but they suffer from a lack of sensitivity to small variations in the level of microstructural homogeneity. Despite this, they can be applied to all two phase systems provided there is adequate contrast between the major and minor phases.

A computer simulation of the technique based on local EDX analysis has shown that it is possible to discern between random dispersions of particles of different volume fractions, between microstructures which exhibit clusters of different sizes, and between microstructures which exhibit clusters of different aspect ratio. This
technique has also been successfully applied to the MMCs of this study. The technique was much more sensitive to small variations in microstructural homogeneity than the techniques based on interparticle spacings and the Dirichlet tessellation. Its universal use is however limited by the chemical composition of the two phases and the positions of the X-ray energy peaks on the EDX spectrum.
Figure 7.1. Schematic showing a method for characterising the interparticle spacings of SiC particles in MMCs.
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Figure 7.2. Histograms showing the distribution of interparticle spacings for longitudinal sections of two MMCs. (a) particle size ratio of 16.67. (b) particle size ratio of 2.94.
Figure 7.3. Histograms showing the normalised distribution of interparticle spacings for longitudinal sections of the two MMCs in figure 7.2. (a) particle size ratio of 16.67. (b) particle size ratio of 2.94.
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Figure 7.4. Plot of the range of the distribution of normalised SiC\textsubscript{p} interparticle spacings against the matrix:reinforcement particle size ratio for longitudinal sections of all MMCs studied.
Figure 7.5. Histograms showing the distribution of normalised interparticle spacings in the through thickness direction of short transverse sections of MMCs. (a) particle size ratio of 13.33. (b) particle size ratio of 2.94. (c) particle size ratio of 1.21.
Figure 7.5. continued.
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Figure 7.6. Histograms showing the distribution of normalised interparticle spacings perpendicular to the through thickness direction of short transverse sections of MMCs. (a) particle size ratio of 13.33. (b) particle size ratio of 2.94. (c) particle size ratio of 1.21.
Figure 7.6. continued.
Figure 7.7. Dirichlet tessellations for typical regions on longitudinal sections of MMCs of matrix:reinforcement particle size ratios of (a) 2.35, (b) 2.76, (c) 13.33 (SiC\(_p\) rich region), and (d) 13.33 (SiC\(_p\) lean region).
Figure 7.7. continued.
Figure 7.8. Plot of the area fraction of clustered Dirichlet cells against the matrix:reinforcement particle size ratio of the MMCs. (note point corresponding to the random distribution, see figure 7.9).

Figure 7.9. Computer simulated random distribution of particles of the area fraction of MMCs in the present study, and its associated Dirichlet tessellation.
Figure 7.10. Histograms showing the distributions of normalised Dirichlet cell areas for the longitudinal sections of MMCs of particle size ratios (a) 2.35, (b) 2.76, and (c) 13.33.
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Figure 7.10. continued.
Figure 7.11. Dirichlet tessellations for regions on short transverse sections of MMCs of particle size ratios (a) 1.21, (b) 2.94, and (c) 13.33.
Figure 7.11. continued.
Figure 7.12. Histograms showing the distributions of normalised Dirichlet cell areas for the short transverse sections of MMCs of particle size ratios (a) 1.21, (b) 2.94, and (c) 13.33.
Figure 7.12. continued.
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Figure 7.13. The Dirichlet tessellations for two regular arrays. (a) square array of points. (b) rectangular array of points with an aspect ratio of 3:1.

Figure 7.14. Plot of Dirichlet cell size versus angle at which measurements were taken for the Dirichlet tessellations for the random array in figure 7.9, and for the regular arrays in figure 7.13.
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Figure 7.15. Flowsheet showing the procedure of the simulation for the characterisation of microstructural homogeneity by local EDX analysis.

Figure 7.16. Computer generated random dispersion of dots with a dot density of 5%.
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Figure 7.17. Computer generated arrays of clusters of dots with overall dot density of 5%. (a) 10x10 clusters. (b) 20x20 clusters. (c) 10x20 clusters. (d) 10x30 clusters.
Figure 7.18. Results of the computer simulation for random dispersions of dots of different dot densities.

Figure 7.19. Results of the computer simulation for arrays of square clusters of different sizes for an overall dot density of 5%.
Figure 7.20. Results of the computer simulation for rectangular clusters of different aspect ratios for an overall dot density of 5%.

Figure 7.21. Actual EDX analysis results for longitudinal sections of the MMCs.
Figure 7.22. As figure 7.21, but the area analysed is normalised by the square of the reinforcement particle size to take into account the change in average interparticle spacing due to changes in particle size.

Figure 7.23. EDX analysis results for short transverse sections of the MMCs normalised as in figure 7.22.
The Effect of the Spatial Distribution of the Reinforcement on the Processing and Heat Treatment of the MMCs

8.1. Processing

None of the materials experienced any form of failure during processing up to and including the hot forging stage. A typical hot forged MMC billet is shown in figure 8.1. It was not until the hot rolling stage that large scale defects were introduced into some of the materials. These manifested themselves as very large edge cracks which initiated at some stage of reduction. The edge cracks became wider and deeper with successive rolling passes down to the required 2mm thickness. Only the unreinforced alloys did not crack on rolling. Figure 8.2 shows a view of the broad face of the unreinforced alloy and that of a typical SiC<sub>p</sub> reinforced sheet.

The formation of edge cracks in the reinforced materials indicates that the presence of the SiC particles must either reduce the ability for the matrix material to flow during hot deformation or that the rolling action introduces voids into the material which cannot be filled by the flowing matrix. For the former to be the case the presence of the reinforcement must have affected the matrix microstructure in terms
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of either its dislocation structure or its precipitate content. The rolling temperature of 748K (475°C), however, would cause annealing of matrix dislocations, and is above the ß phase solvus making the material single phase α-Al, hence no precipitates would exist in either the reinforced or unreinforced conditions. It is therefore suggested that it is the formation of voids into which matrix cannot flow that is the cause of the initiation of edge cracks during rolling.

Examination of rolled materials by reflected light microscopy indicated the presence of voids in the rolled MMCs. Figure 8.3 shows a typical edge crack in a 3μm SiC<sub>p</sub> reinforced alloy. The reinforcement is highly segregated into clusters. The tip of the crack changes direction to propagate through the centre of a region of material rich in reinforcing particles. Likewise, branches of the crack also propagate into reinforcement rich regions. The surface of the crack is very rough, and this roughness often coincides with the boundary between SiC<sub>p</sub> rich and matrix rich regions. Examination of a region of the material close to the crack at higher magnification (figure 8.4) revealed a large amount of porosity which occurred in the clusters of SiC particles. The lack of matrix material in these clusters would mean that these voids could not be filled during flow of the matrix. A situation could therefore be envisaged where the continual initiation and growth of voids, and lack of plastic flow of the matrix could cause the connection of voids to form cracks.

In the central part of the sheet, between the cracked regions on either edge, voids of this nature were not present. MMCs containing the larger grades of SiC<sub>p</sub> however exhibited two other forms of voids. The first is the formation of pores at the interface between the SiC particles and the matrix. This can happen either on one or both sides of the reinforcing particle such that the particles and pores are aligned in the rolling direction, as shown schematically in figure 8.5. Examples of these pores are shown in figure 8.6. The second type of void present in the MMCs with large reinforcing particles forms due to cracking and failure of the reinforcement during mechanical working. Examples of cracked SiC particles are shown in figure 8.7. Neither of these types of voids were present after HIPping, and must therefore have formed during hot forging and/or hot rolling. It will be shown later that these voids
contribute to failure of the MMCs during mechanical testing.

The extent to which edge cracking occurs in the MMCs has been found to be some function of the relative sizes of the SiC\textsubscript{p} reinforcement and the matrix alloy powder. Although no quantitative measurement of the intensity of edge cracking could be produced, it could be seen clearly that as the ratio of matrix:SiC particle sizes increased then edge cracking of the rolled strips became worse. This is shown in figure 8.8. The spatial distribution of the reinforcement was shown above to be controlled by the same particle size ratio. It can therefore be surmised that it is the homogeneity of the distribution of SiC\textsubscript{p} which determines the extent of edge cracking, and just as importantly, the amount of waste material after trimming.

It is not only the extent of edge cracking which is controlled by the particle size ratio, but also the point at which this cracking initiates. Figure 8.9 is a plot of percentage reduction achieved prior to edge crack initiation against the ratio of matrix:SiC particle sizes of the MMCs. It shows that as the particle size ratio increases, and hence as the spatial distribution of the SiC\textsubscript{p} becomes more inhomogeneous, then less reduction in thickness of the MMC can be achieved before initiation of edge cracking occurs.

8.2. Heat Treatment

Microhardness was found to be an impractical method of assessing the ageing process in the matrix of the MMCs. The very small indents required to fit between the reinforcing particles led to considerable variation in microhardness values as a result of the large inaccuracies in the measurement of the dimensions of the indents, and no results are therefore shown. The proximity of the indents to subsurface reinforcement may also have contributed to the large variations in the measured microhardness. The Vickers hardness technique yielded much more reliable results. Despite the interaction of bulk hardness indents with the reinforcement, it was felt that any hardness changes with ageing time could be directly attributed to the matrix
since the SiC<sub>p</sub> is thermally stable at the ageing temperature of 463K (190°C).

The ageing curves for the rolled MMCs and the unreinforced alloy are shown in figure 8.10. All MMCs exhibited a greater hardness than the monolithic material at all stages of the ageing treatment. The greatest peak hardness was achieved in MMCs containing 3μm SiC<sub>p</sub>, and the least hard of the MMCs was that containing 29μm SiC<sub>p</sub>, indicating that as the size of the reinforcing particles was reduced the peak hardness of the MMCs increased. This is supported by the general agreement in the literature that increased strength can be achieved with a reduction in the reinforcement particle size [e.g. Yang et al, 1990, 1991, Mummery, 1991, Geiger and Walker, 1991, Lewandowski et al, 1991, Bhanuprasad et al, 1991]. There was no direct correlation between the matrix:reinforcement particle size ratio, i.e. the homogeneity of the reinforcement within the matrix, and the peak hardness, although in MMCs with the same size of reinforcement a higher level of hardness was achieved when a smaller matrix particle size had been used. All MMCs reached peak hardness after the same ageing time, which was not different to the peak ageing time for the unreinforced alloy. The ageing process was therefore found to be neither accelerated nor delayed by the presence of the reinforcement.

Figure 8.11 shows the variation of the lattice parameter of the α-Al matrix with ageing time for the monolithic Al-4wt%Cu alloy. The lattice parameter increased rapidly at the beginning of the ageing process as copper came out of solid solution. As ageing progressed the rate of change of the lattice parameter with time decreased until it approached the value of the lattice parameter of pure aluminium. Whilst this method was a good indicator that the ageing process was occurring, it gave no indication of what transformations were taking place and at what lengths of time, or where peak ageing occurred. This method of monitoring ageing was therefore discontinued.

DSC traces of samples of rolled unreinforced alloy and MMCs containing either 3μm, 17μm or 29μm SiC<sub>p</sub> are shown in figure 8.12. The solvus temperatures of the matrix phases along with the equilibrium solidus are superimposed on the traces. The
monolithic alloy exhibited a small exothermic peak at 483K (210°C) between the GP zone and \(\theta''\) solvi, a large exothermic peak at 623K (350°C) between the \(\theta''\) and \(\theta'\) solvi, a third exothermic peak at 698K (425°C) between the \(\theta'\) and \(\theta\) solvi, and the beginning of a large endothermic peak at the solidus of the alloy. The MMCs also exhibited this endotherm, and the exothermic peak at 698K (425°C). The large exothermic peak of the unreinforced material at 623K (350°C), however, shifted to the lower temperature of 578K (305°C), and the small exothermic peak at 483K (210°C) was no longer present. The above behaviour of the MMCs was irrespective of the size of the reinforcing particles or of their dispersion within the matrix. The shift of the \(\theta'\) peak to lower temperatures suggests that the precipitation of the \(\theta'\)-phase is accelerated in the MMCs. This is in agreement with Suresh et al [1989]. The loss of the \(\theta''\) peak with the addition of the 20wt% SiC\(_p\) would lead to a delay of ageing since the phase would not precipitate. This deceleration of ageing has also been reported by Kim et al [1992] who attributed it to a low concentration of vacancies following solution treatment.

The absence of any change in the peak ageing time is therefore caused by a deceleration in ageing by the lack of \(\theta''\) precipitates opposed by an acceleration due to the ease of precipitation of the \(\theta'\) phase on dislocations surrounding the reinforcement.

Repeating the DSC experiments for the MMCs in the HIPped condition suggested a different conclusion. The exothermic peak of the precipitation of \(\theta''\) was still suppressed. The peak temperatures for \(\theta'\) precipitation for the HIPped MMCs are shown in table 8.1.
TABLE 8.1. Peak temperature of $\theta'$ precipitation in DSC experiments of the HIPped MMCs

<table>
<thead>
<tr>
<th>Matrix:Reinforcement Particle Size Ratio</th>
<th>$\theta'$ Peak Temperature (K ($^\circ$C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>35:29 (1.21)</td>
<td>297</td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>298</td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>298</td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td>312</td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td>325</td>
</tr>
<tr>
<td>35:- (unreinforced)</td>
<td>345</td>
</tr>
</tbody>
</table>

In this case when the matrix:reinforcement particle size ratio was small, i.e. the microstructure was more homogeneous, the $\theta'$ phase precipitated at temperatures similar to that of the rolled MMCs. When the particle size ratio was much larger, i.e. the microstructure was more segregated, the peak temperature for $\theta'$ phase precipitation was much closer to that of the unreinforced alloy. This effect would lead to an alteration in the time to reach peak hardness during ageing of the HIPped materials with changing level of microstructural homogeneity.

The inhomogeneity experienced by the HIPped MMCs is clearly three-dimensional, whilst that of the rolled MMCs has been shown to be largely two-dimensional. Matrix material, in the rolled MMCs, which is in the centre of the reinforcement free regions is therefore still influenced by the high dislocation density which occurs around the reinforcing particles. Prangnell and Stobbs [1991] have shown that the dislocation density around a reinforcing particle falls with distance from the particle (the absolute distance is normalised by the size of the reinforcing particles). They have also shown that, consequently, after a constant ageing time the $\theta'$ phase precipitates with a decreasing volume fraction with distance from the particle. Matrix material in the centre of a prior matrix particle may therefore be unaffected by the dislocation density around the reinforcement if the microstructure is highly necklaced as in the case of the HIPped materials with the high matrix:reinforcement particle size ratios. This effect is shown schematically in figure 8.13.
8.3. Concluding Remarks

The PM route MMCs of this study survived the hot forging stage of processing without the initiation of visible damage. The presence of the reinforcement, however, caused edge cracking to occur during hot rolling of the MMCs. This edge cracking occurred at lower rolling reductions and was more intense when the matrix:reinforcement particle size ratio was high, that is to say when the reinforcement was poorly distributed in the matrix.

The peak hardness value of the rolled MMCs was predominantly controlled by the size of the reinforcing particles. The peak hardness value increased with diminishing SiC particle size. Overall, the peak hardness was not affected by the matrix:reinforcement particle size ratio, although for a constant reinforcement particle size the materials achieved a greater peak hardness when smaller matrix particles were used to produce the MMCs.

The peak ageing time of the Al-4wt%Cu matrix of the rolled MMCs, aged at 463 K (190°C), was not altered by the addition of 20wt% SiC\textsubscript{p}. The particle size of the reinforcement and the matrix:reinforcement particle size ratio did not affect the peak ageing time. This implies that on a bulk scale ageing is not affected by the variation in spatial distribution of the reinforcement found in these particular MMCs, although it is likely to be affected locally due to small scale variations in reinforcement volume fraction.

Despite the time to reach a peak aged condition being unaltered, the precipitation sequence during ageing was changed by the presence of the reinforcement. The precipitation of $\theta''$ was suppressed, whereas that of $\theta'$ was accelerated. The deceleration in ageing due to the suppression of $\theta''$ was balanced by the acceleration in ageing due to the accelerated precipitation of $\theta'$ resulting in the unaltered time to reach a peak aged condition.

Although the two-dimensional inhomogeneity of the rolled MMCs did not have an
effect on the precipitation sequence, the three-dimensional inhomogeneity of the HIPped materials did. During DSC experiments of the HIPped materials the peak temperature of $\theta'$ phase precipitation was a function of the matrix:reinforcement particle size ratio, and hence the dispersion of the reinforcement within the matrix. As the microstructure of the materials became more homogeneous, the precipitation of the $\theta'$ phase occurred at lower temperatures and thus was accelerated.
Chapter 8. The Effect of the Spatial Distribution of the Reinforcement on the Processing and Heat Treatment of the MMCs

Figure 8.1. Typical forged MMC billet.
Figure 8.2. Rolled sheets of (a) an unreinforced Al-4wt%Cu alloy, and (b) a typical MMC.
Chapter 8. The Effect of the Spatial Distribution of the Reinforcement on the Processing and Heat Treatment of the MMCs

Figure 8.3. Reflected light micrograph of an edge crack in an MMC containing 3μm SiCₚ.

Figure 8.4. Magnified view of a region of material close to the edge crack in figure 8.3.
Figure 8.5. Schematic showing the arrangement of reinforcing particles and interfacial voids (arrowed) in MMCs containing large SiC particles.

Figure 8.6. Reflected light micrograph showing interfacial voids (arrowed) in MMCs containing large SiC particles.
Chapter 8. The Effect of the Spatial Distribution of the Reinforcement on the Processing and Heat Treatment of the MMCs

Figure 8.7. Reflected light micrograph of large SiC particles which have cracked (arrowed) during rolling.

Figure 8.8. Rolled MMC sheets showing the correlation between the intensity of edge cracking after rolling and the matrix:reinforcement particle size ratio. (a) 40:17 (2.35). (b) 50:17 (2.94). (c) 50:3 (16.67).
Chapter 8. The Effect of the Spatial Distribution of the Reinforcement on the Processing and Heat Treatment of the MMCs

Figure 8.9. Plot of percentage reduction achieved prior to edge crack initiation against the matrix:reinforcement particle size ratio.

Figure 8.10. Ageing curves for MMCs and unreinforced Al-4wt%Cu alloy solution treated for 1h at 803 K (530°C), water quenched and aged at 463 K (190°C).
Chapter 8. The Effect of the Spatial Distribution of the Reinforcement on the Processing and Heat Treatments of the MMCs

Figure 8.11. Plot of the variation of the lattice parameter of the $\alpha$-Al matrix with ageing time for the unreinforced Al-4wt%Cu alloy.

Figure 8.12. DSC traces of MMCs containing (a) 29\,\mu m SiC\textsubscript{p}, (b) 3\,\mu m SiC\textsubscript{p} and (c) 17\,\mu m SiC\textsubscript{p}, and (d) an unreinforced alloy. The stable and metastable solvi and the solidus of Al-4wt%Cu are also indicated.
Figure 8.13. Schematic showing the proposed variation in the extent of accelerated precipitation of $\theta'$ with matrix:reinforcement particle size ratio. (a) schematic plot of dislocation density against distance from the matrix/reinforcement interface [after Prangnell and Stobbs, 1991]. (b) the plots in (a) are superimposed on the necklaced matrix particles. (c) The extent of the region of the matrix which exhibits accelerated precipitation of $\theta'$ is indicated.
9.1. Mechanical Testing

Tensile testing was carried out on flat specimens, the gauge of which was 30mm long, 6mm wide and 2mm thick, as in figure 4.1. The cross-head speed was 1mm/min. Typical nominal stress-strain curves for the unreinforced and reinforced materials tested are shown in figure 9.1. Values of the room temperature tensile properties of the MMCs and the unreinforced matrix alloys are given in tables 9.1 and 9.2 respectively. Mechanical testing was performed on specimens in the as rolled, the peak hardened T6 (solution treated and artificially aged), and solution treated and cold water quenched conditions. Testing was carried out on solution treated specimens to remove the influence of matrix precipitates on the mechanical properties of the MMCs and hence to determine only the effect of reinforcement on the mechanical properties.
### TABLE 9.1. Room temperature tensile properties of the MMCs

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Al:SiC&lt;sub&gt;p&lt;/sub&gt; Size Ratio</th>
<th>E (GPa)</th>
<th>UTS (MPa)</th>
<th>σ&lt;sub&gt;0.2%&lt;/sub&gt; (MPa)</th>
<th>ε&lt;sub&gt;f&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Rolled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35:29 (1.21)</td>
<td>89</td>
<td>241</td>
<td>161</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>102</td>
<td>269</td>
<td>171</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>91</td>
<td>236</td>
<td>157</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>50:17 (2.94)</td>
<td>91</td>
<td>276</td>
<td>190</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td>90</td>
<td>302</td>
<td>177</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td>84</td>
<td>321</td>
<td>205</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>Solution Treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 h @ 803 K</td>
<td>35:29 (1.21)</td>
<td>90</td>
<td>282</td>
<td>176</td>
<td>10.4</td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>93</td>
<td>304</td>
<td>157</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>88</td>
<td>276</td>
<td>152</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>50:17 (2.94)</td>
<td>96</td>
<td>293</td>
<td>150</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td>91</td>
<td>379</td>
<td>174</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td>97</td>
<td>369</td>
<td>174</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>Peak Hardened</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 h @ 463 K</td>
<td>35:29 (1.21)</td>
<td>97</td>
<td>305</td>
<td>201</td>
<td>4.3</td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>89</td>
<td>326</td>
<td>204</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>92</td>
<td>305</td>
<td>215</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>50:17 (2.94)</td>
<td>91</td>
<td>314</td>
<td>197</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td>96</td>
<td>366</td>
<td>224</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td>93</td>
<td>362</td>
<td>223</td>
<td>7.4</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 9.2. Room temperature tensile properties of the unreinforced alloys

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Powder Size (μm)</th>
<th>E (GPa)</th>
<th>UTS (MPa)</th>
<th>σ&lt;sub&gt;0.2%&lt;/sub&gt; (MPa)</th>
<th>ε&lt;sub&gt;f&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Rolled</td>
<td>35</td>
<td>74</td>
<td>217</td>
<td>135</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>70</td>
<td>196</td>
<td>110</td>
<td>16.3</td>
</tr>
<tr>
<td>Solution Treated</td>
<td>35</td>
<td>71</td>
<td>247</td>
<td>104</td>
<td>18.8</td>
</tr>
<tr>
<td>1.0 h @ 803 K</td>
<td>80</td>
<td>75</td>
<td>248</td>
<td>97</td>
<td>26.4</td>
</tr>
<tr>
<td>Peak Hardened</td>
<td>35</td>
<td>73</td>
<td>309</td>
<td>189</td>
<td>11.7</td>
</tr>
<tr>
<td>12 h @ 463 K</td>
<td>80</td>
<td>72</td>
<td>314</td>
<td>200</td>
<td>17.0</td>
</tr>
</tbody>
</table>

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In general, the elastic modulus, \( E \), of the reinforced materials was approximately 26% higher than that of the unreinforced alloy. All but four of the values of Young's modulus for the MMCs lie within the upper (129.4 GPa) and lower (90.3 GPa) bounds as calculated using equations 2.11 and 2.12 in section §2.6.4.1. For the purposes of the calculations of the upper and lower bound values, the Young's moduli of the matrix and reinforcement were assumed to be 70 GPa and 400 GPa respectively. The spread in values of the elastic moduli of the MMCs is probably due to the errors in measuring the initial slope of the stress-strain curves. These errors occur because the linear portion of the stress-strain curves of the MMCs is much less extensive than in the unreinforced materials. After quenching the residual stress in the matrix due to differential thermal expansion causes the matrix to be in tension prior to testing. Localised premature yielding therefore occurs on the application of a further tensile stress during testing. This localised yielding causes a deviation from linearity in the early stages.

The ultimate tensile strength of the MMCs was also considerably higher than the unreinforced material in all three conditions. No correlation was established between the alloy:SiC\(_p\) particle size ratio and UTS, although the size of the SiC particles alone did affect the UTS. This is in agreement with numerous other researchers (see section §2.6.4.2) Similar behaviour was observed when considering the 0.2% proof stress, although the correlation between proof stress and SiC particle size is less evident. There was no apparent relationship between the ductility of the MMCs and either the particle size of the SiC\(_p\) or the alloy:SiC\(_p\) particle size ratio. Elongations to failure of the MMCs were generally less than half of that of the monolithic material in both conditions, despite the extra ductility that the solution treatment imparts.

The matrix grain sizes of the as rolled MMCs and unreinforced alloys are given in table 9.3, along with the predicted recrystallised grain sizes from equations 2.5 and 2.6 in section §2.6.2.3.
Chapter 9. The Effect of the Spatial Distribution of the Reinforcement on the Tensile Properties of the MMCs

**TABLE 9.3.** Grain sizes in the as rolled MMCs and unreinforced alloys predicted recrystallised grain sizes for the MMCs

<table>
<thead>
<tr>
<th>Matrix:SiC&lt;sub&gt;p&lt;/sub&gt; Particle Size Ratio</th>
<th>Measured Grain Size (μm)</th>
<th>Particle Stimulated Grain Size&lt;sup&gt;+&lt;/sup&gt; (μm)</th>
<th>Growth Limited Grain Size&lt;sup&gt;↑&lt;/sup&gt; (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35:29 (1.21)</td>
<td>48</td>
<td>51.4</td>
<td>107.4</td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>41</td>
<td>30.1</td>
<td>63.0</td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>50</td>
<td>51.4</td>
<td>107.4</td>
</tr>
<tr>
<td>50:17 (2.94)</td>
<td>39</td>
<td>30.1</td>
<td>63.0</td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td>90</td>
<td>5.3</td>
<td>11.1</td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td>94</td>
<td>5.3</td>
<td>11.1</td>
</tr>
<tr>
<td>35:- (unreinforced)</td>
<td>120</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>80:- (unreinforced)</td>
<td>135</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

<sup>+</sup> from equation 2.5.  
<sup>↑</sup> from equation 2.6.

The measured grain sizes of the as rolled MMCs containing 17μm or 29μm SiC<sub>p</sub> are closer to the predicted grain sizes due to particle stimulated nucleation than those limited by grain growth. This is in agreement with the proposal by Humphreys *et al*, [1990] that the recrystallised grain size of MMCs containing particles greater than 5μm in diameter will be controlled by particle stimulated nucleation rather than pinning of the grain boundaries during grain growth. The measured grain sizes of the MMCs containing 3μm SiC<sub>p</sub> particles were much larger than either of the predicted recrystallised grain sizes.

More importantly, a combination of the measured grain sizes of the as rolled MMCs and the 0.2% proof strength and UTS data in table 9.1 indicates that the effect of the matrix grain size on the strength of the MMCs was very weak in comparison to the influence of the reinforcement particle size. This is highlighted by the data for the MMCs containing 3μm SiC<sub>p</sub>, which had the largest grain sizes but exhibited the highest UTS and 0.2% proof strengths.

Above it was shown that the matrix:SiC particle size ratio had little or no effect on
the mechanical properties of the MMCs. Instead it was the size of the reinforcing particles which had the strongest effect. The strong influence of reinforcement particle size on the strength of MMCs was discussed in section §2.6.4.2. The lack of homogeneity found in the broad face of the rolled MMCs was much less evident in the transverse directions. Since the mechanical properties were determined by loading along the rolling direction, and failure occurred through the thickness of the material, it is perhaps not surprising that the particle size ratio had little effect. In the present work the determination of the spatial distribution of the reinforcement has been done on the longitudinal and short transverse planes of the rolled sheet separately, and the present techniques are not able to identify the spatial distributions of reinforcement in materials which exhibit different textures in different orientations, i.e. they do not yield three dimensional information. Techniques which could, perhaps, be developed to further this end, such as X-ray tomography, currently lack the necessary resolution for spatial distributions of this kind. It could be suggested that the planar methods employed in this study should be repeated either in random or pre-determined planes within the material. Such methods are, however, extremely time consuming. Future work should consider in which plane the spatial distribution of reinforcement would be most influential and make some determination of homogeneity in this single orientation.

Despite the poor correlation between the microstructure of the rolled strips and their mechanical properties, examination of the fracture surfaces of tensile specimens reveals a number of interesting features. Figure 9.2 shows the fracture surface of an unreinforced specimen. It shows an even distribution of dimples, of approximately 10\(\mu\)m in size, indicative of a ductile failure. Figures 9.3 and 9.4 show the fracture surfaces of the 17\(\mu\)m and 29\(\mu\)m SiC\(_p\) reinforced MMCs respectively. In both cases, ductile dimples are still present, but now contain reinforcing particles and the size of the dimples depends on the size of the reinforcing particles. Between these large particle containing dimples there are small ductile dimples of the size of those present in the unreinforced material, and are probably formed due to ductile failure of the matrix between the reinforcement. The particles inside the large dimples have flat faces which indicates that they have fractured. Combining this with the knowledge
that particles fail during deformation of the material, it can be concluded that the ductile dimples around the particles have been nucleated at the voids created by the failure of the particles during processing or testing. The above are in agreement with the results of Mummery [1991]. To confirm that failure of the larger reinforcing particles did occur during tensile testing longitudinal sections of post test MMC specimens were metallographically prepared. Particles were found to have failed all along the gauge length of the specimens (see figure 9.5), although a higher density of failed reinforcing particles were observed close to the fracture surface (figure 9.5b). This agrees with the findings of Llorca et al, [1993] and Singh and Lewandowski, [1993].

The fracture surfaces of the MMCs containing 3µm SiC particles were somewhat different. Ductile dimples were still present (figure 9.6), with a large proportion containing reinforcing particles. The size of the dimples was again of the order of the size of the reinforcing particles and thus was smaller than in the unreinforced specimens. This time the particles inside the dimples were whole indicating that they did not fail during deformation of the MMC. This again is in agreement with Mummery's work. More importantly to this study, several other features were present on the fracture surfaces of the composites containing 3µm SiC<sub>p</sub>. Figure 9.7 shows a uniform fracture surface in which there is a string of larger dimples of the size found in the unreinforced material. This string of dimples lies perpendicularly to the thickness of the material. This suggests the presence of thin layers of material which do not contain any reinforcement. One could imagine this being caused by a large matrix particle being rolled flat during processing. If this particle was heavily necklaced then this thin layer of matrix would be sandwiched by layers of SiC<sub>p</sub> rich material. These thin layers could also be seen in the optical microscope prior to testing (figure 9.8). More evidence for the presence of these thin layers of unreinforced material is presented in figure 9.9, where a small portion of material has failed parallel to the broad face of the material, which is perpendicular to the usual direction of failure i.e. failed in the same plane as the proposed unreinforced layers. This failure has no SiC particles on the surface. It is therefore suggested that the failure has occurred between a layer devoid of reinforcement and a layer rich in
reinforcement. The mechanism of formation and failure of these layers is shown schematically in figure 9.10.

A final feature of the failure of the MMCs containing 3\(\mu\)m \(\text{SiC}_p\) is multiple crack initiation before final failure. Figure 9.11 shows the edge of failed tensile specimens just below the fracture surface for (a) a monolithic material, and (b) an MMC containing 3\(\mu\)m \(\text{SiC}_p\). That of the unreinforced material is highly deformed and necked, but there is no sign of any flaws other than the fracture surface itself. Failed tensile specimens of MMCs containing 17\(\mu\)m and 29\(\mu\)m \(\text{SiC}_p\) exhibited little necking. Figure 9.11b indicates that like the MMCs containing the larger grade of SiC, the failed specimen of the 3\(\mu\)m \(\text{SiC}_p\) containing MMC exhibits little or no necking, but a number of cracks have initiated below the fracture surface prior to failure.

The features of the fracture of MMC tensile specimens discussed here, together with the conclusion that edge crack initiation and edge crack intensity during rolling are dependent on the spatial distribution of the \(\text{SiC}_p\) reinforcement, suggest that although the tensile properties of particulate MMCs may not be very sensitive to the inhomogeneity of reinforcement at the scales determined in this study, the fracture properties such as toughness may be.

9.2. Fracture Toughness

9.2.1. Plane Strain Thickness Criteria

The measured value of fracture toughness for a given material is dependent upon the geometry of the specimen, the thickness most importantly. For a comparable plane strain fracture toughness to be measured the thickness of the tested specimen must comply with the plane strain thickness criterion

\[ B > 2.5 \left( \frac{K_{IC}}{\sigma_y} \right)^2 \quad ...(9.1) \]

where \(B\) is the thickness of the material, \(K_{IC}\) is the plane strain mode I fracture toughness.
Chapter 9. The Effect of the Spatial Distribution of the Reinforcement on the Tensile Properties of the MMCs

toughness, and \( \sigma_y \) is the yield stress of the material.

If the validity of a test, in terms of fulfilling the plane strain thickness criterion, is to be determined prior to performing the test then an estimate of the fracture toughness of the material must be sought. The validity of fracture toughness data in the literature has been reviewed by Goolsby and Austin [1989] and Roebuck and Lord [1990], and measurements of \( K_{IC} \), for a number of discontinuous SiC reinforced aluminium alloys, which fulfil the plane strain thickness criterion are given in table 9.4 below [Goolsby and Austin, 1989].

<table>
<thead>
<tr>
<th>Material System</th>
<th>( K_{IC} ) (MPam(^{1/2}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rolled 25% SiC(_p)/7090</td>
<td>8</td>
<td>Goolsby and Austin, 1984</td>
</tr>
<tr>
<td>Extruded 30% SiC(_p)/7091</td>
<td>14</td>
<td>Austin and Goolsby, 1986</td>
</tr>
<tr>
<td>Extruded 20% SiC(_p)/6061</td>
<td>15</td>
<td>Goolsby and Austin, 1989</td>
</tr>
<tr>
<td>Rolled 25% SiC(_p)/6061</td>
<td>16</td>
<td>Goolsby and Austin, 1989</td>
</tr>
<tr>
<td>Extruded 20% SiC(_p)/MB78</td>
<td>16</td>
<td>Shang et al, 1988</td>
</tr>
<tr>
<td>Rolled 30% SiC(_p)/7091</td>
<td>18</td>
<td>Austin and Goolsby, 1986</td>
</tr>
<tr>
<td>Cast/HIPped 20% SiC(_p)/A357</td>
<td>19</td>
<td>Austin and Saathoff, 1988</td>
</tr>
<tr>
<td>Extruded 15% SiC(_p)/2124</td>
<td>21</td>
<td>Marchand et al, 1988</td>
</tr>
<tr>
<td>Cast/HIPped 10% SiC(_p)/A357</td>
<td>21</td>
<td>Austin and Saathoff, 1988</td>
</tr>
</tbody>
</table>

Using equation 9.1 and the data in tables 9.1 and 9.4 we can determine the minimum thickness of material required for all of the MMCs to yield reliable plane strain fracture toughnesses. If the fracture toughness of the MMCs was the maximum value in table 9.4 then for all of them to fracture under plane strain conditions they would have to obey the criterion \( B > 49 \) mm. Since the thickness of the materials under study was 2 mm it is clear that none of the MMCs would fail yielding plane strain fracture toughnesses. If the fracture toughness of the materials was the minimum value in table 9.4 then for all of them to fracture under plane strain conditions the
criterion $B > 7.1$ mm must be obeyed. Again none of the specimens would fail under plane strain conditions. Even if this condition was obeyed the values still could not be compared with the unreinforced specimens since the plain strain thickness criterion for unreinforced aluminium alloys is typically $B > 664$ mm ($K_{IC} = 50$ MPam$^{1/2}$ typically). For a thickness of 2 mm the maximum fracture toughness values under plane strain conditions for the MMCs in this study are shown in table 9.5.

**TABLE 9.5. Calculated maximum plane strain fracture toughnesses for the MMCs**

<table>
<thead>
<tr>
<th>Matrix:Reinforcement Particle Size Ratio</th>
<th>Condition</th>
<th>Maximum $K_{IC}$ (MPam$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35:29</td>
<td>As Rolled</td>
<td>4.55</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>4.98</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>5.69</td>
</tr>
<tr>
<td>40:17</td>
<td>As Rolled</td>
<td>4.84</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>4.44</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>5.77</td>
</tr>
<tr>
<td>80:29</td>
<td>As Rolled</td>
<td>4.44</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>4.30</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>6.08</td>
</tr>
<tr>
<td>50:17</td>
<td>As Rolled</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>5.57</td>
</tr>
<tr>
<td>40:3</td>
<td>As Rolled</td>
<td>5.01</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>4.92</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>6.36</td>
</tr>
<tr>
<td>50:3</td>
<td>As Rolled</td>
<td>5.80</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>4.92</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>6.31</td>
</tr>
</tbody>
</table>

All of these maximum values are significantly below the smallest value in table 9.4. For comparison between the fracture toughness of the MMCs with those of the
unreinforced materials the $K_{IC}$ of the monolithic alloys could not be greater than the values given in table 9.6. All of these values are an order of magnitude smaller than the typical value for aluminium alloys.

**TABLE 9.6.** Calculated maximum plane strain fracture toughnesses for the unreinforced matrix alloys.

<table>
<thead>
<tr>
<th>Powder Size (µm)</th>
<th>Condition</th>
<th>Maximum $K_{IC}$ (MPam$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>As Rolled</td>
<td>3.11</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>2.74</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>5.66</td>
</tr>
<tr>
<td>35</td>
<td>As Rolled</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td>Solution Treated</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td>Peak Aged</td>
<td>5.35</td>
</tr>
</tbody>
</table>

It is clear then that plane strain fracture toughness testing could not be carried out since the materials could not comply with the plane strain thickness criterion. A simple comparative measure of toughness was therefore required, and since tensile specimens had already been produced it was proposed that notches should be cut into the tensile specimens, so that notched tensile data could be generated. The practice of testing notched tensile specimens has been adopted by the Structural Materials Centre at DRA Farnborough [Shakesheff$^{a,b}$, 1993]. The specimen geometry used in this study was the same as that used by the DRA.

**9.2.2. Notch Effects**

The presence of a notch in a material increases the tendency for brittle fracture in four ways [Dieter, 1986]:

- By producing high local stresses
- By producing high local strain hardening and cracking
By producing a local strain rate magnification
By introducing a triaxial tensile stress state.

It is the latter of these that can be exploited for the assessment of the fracture properties of a material by notch tensile testing. The elastic stress distribution ahead of a notch in a thin plate is shown schematically in figure 9.12. When the plate is loaded in the y-direction to a stress below the elastic limit of the material then the distribution of stress in the y-direction, \( \sigma_y \), would be as shown in figure 9.12. At the same time a transverse elastic stress, \( \sigma_x \), is produced by the geometry of the notch. This can be understood in physical terms if we imagine a series of microscopic tensile specimens at the tip of the notch. If each of these specimens were able to deform freely they would undergo a tensile strain, \( \epsilon_y \), in response to the local value of \( \sigma_y \). Since \( \sigma_y \) falls off rapidly with distance from the notch root, there will be an elastic strain gradient ahead of the notch. Each tensile strain \( \epsilon_y \) will also have associated with it a lateral contraction \( \epsilon_x \) due to Poisson's ratio, \( \nu \). If each tensile element is free to deform independently of its neighbours, \( \epsilon_x \) is given by

\[
\epsilon_x = -\nu \epsilon_y \tag{9.2}
\]

Thus, all of the interfaces between the tensile elements would pull apart. In order to maintain continuity a tensile stress \( \sigma_x \) must exist across each interface. At the free surface of the notch \((x=0)\) the tensile element can undergo lateral contraction without any restraint from one side and \( \sigma_x = 0 \). The necessary lateral stress to maintain continuity increases with distance from the notch root, but it decreases at large values of \( x \) because the difference in longitudinal strain between adjacent elements becomes small as the \( \sigma_y \) distribution plateaus out. \( \sigma_x \) will rise steeply with \( x \) and then fall more slowly as indicated in figure 9.12.

The transverse stresses raise the average value of longitudinal stress at which yielding occurs. For a Tresca yield criterion, \( \sigma_0 = \sigma_1 - \sigma_3 \) where \( \sigma_0 \) is the yield strength of the material, \( \sigma_1 \) is the principal tensile stress in the longitudinal direction, and \( \sigma_3 \) is the transverse principal stress. In an unnotched tensile specimen the longitudinal stress alone measures yielding since \( \sigma_0 = \sigma_1 - 0 \). In a notched specimen yielding starts at the
root of the notch because \( \sigma_z = 0 \) at this free surface, but just ahead of the notch \( \sigma_0 = \sigma_y - \sigma_x \). The inherent material yield strength is the same whether notched or unnotched so it takes a higher value of longitudinal stress to produce yielding in a notched specimen.

As a result of the triaxial stress state produced by the notch the general yield stress of a notched specimen is greater than the uniaxial yield strength \( \sigma_0 \) because it is more difficult to spread the yielded zone in the presence of triaxial stresses. The ratio of notched to unnotched flow stress is referred to as the "plastic constraint factor". Thus in a ductile material the triaxial stress state of a notch results in "notch strengthening" i.e. the plastic constraint factor is greater than unity. In a material prone to brittle fracture the increased tensile stresses from the plastic constraint can exceed the critical value for fracture before the material undergoes general plastic yielding, and hence the plastic constraint factor is less than one. The difficulty in the spreading of the yielded zone due to the triaxial stress state also raises the tensile strength of the material, and therefore the ratio of the notched to unnotched UTS can also be used as a measure of notch sensitivity in the same way as the plastic constraint factor.

9.2.3. Notched Tensile Properties

Notched tensile data for the MMCs and the unreinforced alloys are given in tables 9.7 and 9.8 respectively.
### TABLE 9.7. Room temperature notched tensile properties of the MMCs

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Al:SiC&lt;sub&gt;p&lt;/sub&gt; Size Ratio</th>
<th>UTS (MPa)</th>
<th>α&lt;sub&gt;0.2%&lt;/sub&gt; (MPa)</th>
<th>ε&lt;sub&gt;f&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Rolled</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35:29 (1.21)</td>
<td>214</td>
<td>214</td>
<td>214</td>
<td>0.26</td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>251</td>
<td>215</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>214</td>
<td>191</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>50:17 (2.94)</td>
<td>253</td>
<td>235</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td>299</td>
<td>240</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td>313</td>
<td>288</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Solution Treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35:29 (1.21)</td>
<td>241</td>
<td>212</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>254</td>
<td>194</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>228</td>
<td>186</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>50:17 (2.94)</td>
<td>241</td>
<td>186</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td>320</td>
<td>192</td>
<td>2.14</td>
<td></td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td>310</td>
<td>214</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>1 h @ 803 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35:29 (1.21)</td>
<td>283</td>
<td>283</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>40:17 (2.35)</td>
<td>300</td>
<td>271</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>80:29 (2.76)</td>
<td>278</td>
<td>261</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>50:17 (2.94)</td>
<td>341</td>
<td>268</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>40:3 (13.33)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50:3 (16.67)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 9.8. Room temperature notched tensile properties of the unreinforced alloys

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Powder Size (μm)</th>
<th>UTS (MPa)</th>
<th>α&lt;sub&gt;0.2%&lt;/sub&gt; (MPa)</th>
<th>ε&lt;sub&gt;f&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Rolled</td>
<td>35</td>
<td>229</td>
<td>166</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>217</td>
<td>132</td>
<td>9.5</td>
</tr>
<tr>
<td>Solution Treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>275</td>
<td>154</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>278</td>
<td>124</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>1 h @ 803 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>346</td>
<td>253</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>345</td>
<td>234</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Peak Hardened</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>346</td>
<td>253</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>345</td>
<td>234</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>12 h @ 463 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results of the notched tensile tests show similar trends to the results of the unnotched tensile tests outlined in section §9.1. Generally, as the size of the reinforcing particles increases then both the 0.2% proof stress and the UTS fall. There is no correlation between either the 0.2% proof stress or the UTS and the matrix:reinforcement particle size ratio, indicating that the variation in the spatial distribution of the reinforcement exhibited by these MMCs has no effect on the notched tensile behaviour. The elongation to failure was independent of both the size of the reinforcing particles and the matrix:reinforcement particle size ratio.

Figure 9.13 is a plot of the notched 0.2% proof stress against the unnotched 0.2% proof stress for all of the MMCs and the unreinforced alloys. It clearly shows that the notched proof stress rises linearly with increasing unnotched proof stress with the notched proof stress being larger than the unnotched value for all of the materials. This indicates that a triaxial stress state existed in the notched tensile specimens and therefore that these tests could help to assess the toughness of the materials. This is supported by a similar trend between the notched and unnotched UTS (see figure 9.14)

Figure 9.15 is a plot of the notched elongation to failure against the unnotched elongation to failure. This shows that the presence of the notch generally causes a reduction in the ductility in the materials. There is an apparent relationship between the notched ductility and the unnotched ductility for materials which had elongations to failure greater than 10% in the unnotched condition. Below this regime, the poor notched elongation to failure was largely unaffected by the unnotched elongation to failure. However it should be noted that the materials which show a notched elongation to failure of approximately 4% and greater in figure 9.15 are unreinforced alloys, and hence it appears that the notched ductility of the MMCs is unaffected by their unnotched ductility while there is an approximate linear relationship between the notched elongation to failure and the unnotched elongation to failure for the unreinforced alloys.

In section §9.2.2 it was shown that notch sensitivity can be used as a measure of the
toughness of a material. The important parameter was said to be the ratio of the notched yield stress to the unnotched yield stress (plastic constraint factor), or the ratio of the notched UTS to the unnotched UTS. Kaufman and Johnson [1962] showed that the expected correlation between these parameters and the in service performance of the materials was poor. The toughness of aluminium alloys generally falls with an increase in strength, and Kaufman and Johnson found that there was no influence of the strength of an aluminium alloy on its notched to unnotched strength ratios, and hence the ratios did not adequately represent the toughness of the materials. Figures 9.16 and 9.17 are plots of the notched to unnotched proof stress ratio and the notched to unnotched UTS ratio, respectively, against proof stress for the materials of this study. They confirm that there is little influence of the unnotched strength, and hence toughness, on the notched to unnotched strength ratios.

Kaufman and Johnson suggested that a better indicator of toughness was the ratio of the notched UTS to the unnotched yield strength. Their reasoning behind this is twofold. Firstly, they indicate that the failure of a "low ductility" type depends upon whether plastic deformation takes place, that is to say whether the net stress exceeds the yield strength of the material. Secondly, the notched UTS always occurs before the maximum in the stress-strain curve due to premature failure, and therefore the notched UTS is controlled by the extent of plastic deformation in the notched sample. Kang and Grant [1985] support the suggestion of Kaufman and Johnson. They have found that this revised strength ratio increases linearly with decreasing tensile strength for a number of unreinforced aluminium alloys, and hence that this strength ratio increases with increasing toughness.

Shakesheff\(^a\)\(^b\) [1993] found that the ratio of the notched UTS to the unnotched yield strength is also a good indicator of toughness for SiC\(_p\) reinforced aluminium alloys. Figure 9.18 shows the relationship between the unnotched proof stress and the ratio of the notched UTS to the unnotched proof stress for the materials of this study, along with the data from the Defence Research Agency (DRA) [Shakesheff\(^a\), 1993]. Although there is a large amount of scatter in the data, figure 9.18 shows that there
is a general increase in this strength ratio with decreasing proof stress (increasing toughness) for all the data, and this relationship also appears to hold for the materials under different heat treated conditions. The relationship does not appear to be of the same form as the data from DRA. More recent DRA data [Shakesheff, 1993] indicates that the strength ratio varies more sharply at lower values of proof stress. With this in mind the data from this study now shows better agreement with the DRA data for the materials with proof stresses greater than 110 MPa with the strength ratio increasing much more sharply for materials with proof stresses lower than 110 MPa.

Now that the best parameter for the assessment of toughness from notched tensile tests has been established, the effect of the spatial distribution of the reinforcement on the toughness of the MMCs should be considered. Figure 9.19 is a plot of the ratio of notched UTS to unnotched proof stress against the matrix:reinforcement particle size ratio. It shows a trend of decreasing notch sensitivity with increasing matrix:reinforcement particle size ratio, which implies a decrease in toughness as the reinforcement becomes more homogenously distributed throughout the matrix of the MMCs. This conclusion is only tentative however. The materials which show the lowest notch sensitivity and have the highest matrix:reinforcement particle size ratio are the MMCs which contain 3μm SiC particles. Hence, the low notch sensitivity at higher particle size ratios could have been influenced more by the size of the reinforcing particles and also the different failure mechanism of these MMCs from those containing the larger particles.

9.3. Concluding Remarks

Although the rolled MMCs exhibited a wide range of microstructural homogeneity in two dimensions, all of them showed a low level of segregation of the reinforcement in three dimensions. The segregation therefore, was of a scale which did not appear to affect the tensile properties the MMCs in either unnotched or notched specimens. It was the reinforcement particle size which had the major influence over the strength
Chapter 9. The Effect of the Spatial Distribution of the Reinforcement on the Tensile Properties of the MMCs

of the MMCs.

Examination of the fracture surfaces of the failed test pieces indicated that the spatial distribution of the reinforcement gave rise to some anomalous effects in the mechanism of failure. "Stringers" of large ductile dimples, of similar diameter to those found in the fracture surfaces of the unreinforced materials, were found in the fracture surfaces of MMCs with high matrix:reinforcement particle size ratios. These stringers were of the same dimensions as the thin layers of reinforcement free material in the microstructures of transverse sections of these particular MMCs. It can be concluded therefore that these stringers formed by the ductile failure of the reinforcement free layers. The same fracture surfaces also showed signs of delamination occurring between the matrix rich and reinforcement rich layers. A final feature of the failure of the MMCs with high matrix:reinforcement particle size ratios was the presence of multiple cracking below the fracture surface which initiated prior to final failure of the specimens.

The anomalous features on fracture surfaces and the multiple cracking of some materials during testing, together with the effect of edge cracking during rolling (section 8.1), suggest that the spatial distribution of the reinforcement affects the fracture properties of the MMCs. The results of notched tensile testing showed, in agreement with other workers, that the best indicator of notch sensitivity, and hence toughness, was the ratio of notched UTS to unnotched proof stress. It was found that as the matrix:reinforcement particle size ratio increased (i.e. the reinforcement became more segregated), the notch sensitivity decreased (toughness increased), although a possible reinforcement size effect makes this conclusion uncertain.
Chapter 9. The Effect of the Spatial Distribution of the Reinforcement on the Tensile Properties of the MMCs

Figure 9.1. Typical stress-strain curves for the MMCs and the unreinforced Al-4wt%Cu alloy.

Figure 9.2. SEM secondary electron micrograph of the fracture surface of a failed unreinforced Al-4wt%Cu alloy tensile specimen.
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Figure 9.3. SEM secondary electron micrograph of the fracture surface of a failed MMC tensile specimen containing 17μm SiC$_p$.

Figure 9.4. SEM secondary electron micrograph of the fracture surface of a failed MMC tensile specimen containing 29μm SiC$_p$.
Figure 9.5. Reflected light micrographs of sections of a failed tensile test specimen showing a higher proportion of cracked reinforcing particles close to the fracture surface (a) than remote from it (b).
Figure 9.6. SEM secondary electron micrograph of the fracture surface of a failed MMC tensile specimen containing 3μm SiCₚ.

Figure 9.7. SEM secondary electron micrograph of the fracture surface of a failed MMC tensile specimen containing 3μm SiCₚ, showing stringers of large ductile dimples.
Figure 9.8. Reflected light micrograph of a short transverse section of an MMC containing 3\(\mu\)m SiC\(_p\) showing thin layers of matrix between layers of SiC\(_p\) rich material.

Figure 9.9. SEM secondary electron micrograph of the fracture surface of a failed MMC tensile specimen containing 3\(\mu\)m SiC\(_p\) showing regions of delamination.
The Effect of the Spatial Distribution of the Reinforcement on the Tensile Properties of the MMCs

Figure 9.10. Schematic showing the formation and failure of thin layers of matrix between layers of SiC\textsubscript{p} rich material.
Figure 9.11. SEM secondary electron micrographs of the edges of failed tensile specimens below the fracture surfaces. (a) unreinforced Al-4wt%Cu alloy. (b) MMC containing 3μm SiCp.
Figure 9.12. Schematic showing the variation of stress ahead of a notch in a thin sheet. [after Dieter, 1986].
Chapter 9. The Effect of the Spatial Distribution of the Reinforcement on the Tensile Properties of the MMCs

Figure 9.13. Plot of notched 0.2% proof stress against unnotched 0.2% proof stress for all of the materials studied.

Figure 9.14. Plot of notched UTS against unnotched UTS for all of the materials studied.
Figure 9.15. Plot of notched elongation to failure against unnotched elongation to failure for all of the materials studied.
Figure 9.16. Plot of notched:unnotched 0.2% proof stress ratio against unnotched 0.2% proof stress for all of the materials studied.

Figure 9.17. Plot of notched:unnotched UTS ratio against unnotched 0.2% proof stress for all of the materials studied.
Figure 9.18. Plot of the ratio of notched UTS to unnotched 0.2% proof stress against unnotched 0.2% proof stress for all of the materials studied.
Figure 9.19. Plot of the ratio of notched UTS to unnotched 0.2% proof stress against matrix: reinforcement particle size ratio.
10.1. Conclusions

1. The microstructures of the MMCs in the HIPped condition exhibited necklacing of prior matrix particles by the SiC\textsubscript{p} reinforcement. The severity of this necklacing increased as the ratio of matrix:reinforcement particle size ratio increased.

2. The microstructures of the rolled MMCs were formed by the deformation of their associated microstructures after HIPping. The level of necklacing in the microstructures of the HIPped MMCs, and hence the origin of microstructural inhomogeneity in the rolled materials, has been described in terms of the conversion of the volume fraction of reinforcement to the number fraction of reinforcing particles, and in terms of the ideal packing of rigid spheres. The attachment of reinforcing particles to the softer matrix particles during blending also contributed to the necklaced microstructures after HIPping.
3. After rolling, the microstructures of the MMCs all showed some level of segregation of the reinforcement on the longitudinal plane. The extent of this segregation also increased with increasing matrix:reinforcement particle size ratio. The microstructures on the transverse planes of the rolled sheets were more homogeneous than their respective microstructures on the longitudinal plane, although the reinforcement appeared to be in layers with thin layers devoid of reinforcement in between. This suggests that the microstructural inhomogeneity was largely two-dimensional.

4. Three practical techniques for the characterisation of the dispersion of reinforcement in discontinuously reinforced MMCs have been discussed. The first is the determination of the range of the distribution of interparticle spacings on linear intercepts of the microstructure. The second is the determination of the range of cell sizes measured from the Dirichlet tessellation constructed from the MMC microstructure. The third technique measures the variation in local chemical composition by EDX analysis.

5. The variation of the spatial distribution of the reinforcement is determined by local interparticle distances. For a constant volume fraction of reinforcement the mean distance between particles rises with increasing particle diameter, and therefore MMCs which have different reinforcement particle sizes will show local interparticle distances which are dependent on both the level of microstructural homogeneity and the size of the reinforcing particles. The techniques for characterisation of spatial distributions therefore normalise in some way for the variation in interparticle spacing with particle size.

6. The techniques using the distribution of interparticle spacings and the distribution of Dirichlet cell sizes were applied successfully to the PM route MMCs of this study for large scale differences in the dispersion of the reinforcement, but they suffered from a lack of sensitivity to small variations in the level of microstructural homogeneity. The techniques are based on measurements taken directly from the microstructure, and so despite their lack
of sensitivity they can be applied to all two phase systems provided there is adequate image contrast between the major and minor phases.

7. A computer simulation of the technique based on local EDX analysis has shown that it may be possible to discern between random dispersions of particles of different volume fractions, between microstructures which exhibit clusters of different sizes, and between microstructures which exhibit clusters of different aspect ratio.

8. The technique based on local EDX analysis has also been applied successfully to the MMCs of this study. This technique was more sensitive to small variations in the microstructure than the techniques based on interparticle spacings and the Dirichlet tessellation. Its universal use is however limited by the chemical composition of the two phases and the positions of the X-ray energy peaks on the EDX spectrum.

9. The PM route MMCs of this study survived the hot forging stage of processing without being visibly damaged. The presence of the reinforcement caused edge cracking to occur during hot rolling of the MMCs. This edge cracking was more intense and initiated at an earlier stage when the matrix:reinforcement particle size ratio was high, that is to say when the reinforcement was poorly distributed in the matrix.

10. The peak hardness of the MMCs was predominantly controlled by the size of the reinforcing particles. The peak hardness increased with diminishing SiC particle size. Generally, the peak hardness was not affected by the matrix:reinforcement particle size ratio, although for a constant reinforcement particle size the materials achieved a slightly greater peak hardness when smaller matrix particles were used to produce the MMCs.

11. The time to reach peak hardness of the Al-4wt%Cu matrix, aged at 463 K (190°C), was not altered by the addition of 20wt% SiC. Neither the size of
the reinforcing particles nor the matrix:reinforcement particle size ratio affected the peak ageing time. This implies that on a bulk scale the time to reach peak hardness was not influenced by the variation in spatial distribution of the reinforcement found in these particular MMCs, although it is likely to be affected on a small scale due to local variations in volume fraction.

12. Despite the time to reach peak ageing in the rolled MMCs being unaltered, the precipitation sequence during the heat treatment was changed by the presence of the reinforcement. The precipitation of the $\theta''$ phase was suppressed causing a deceleration in ageing. DSC experiments showed that the $\theta'$ phase precipitated at lower temperatures and hence the precipitation was accelerated. The deceleration in ageing due to the suppression of $\theta''$ was balanced by the acceleration in ageing due to the accelerated precipitation of $\theta'$ resulting in the unaltered peak ageing time.

13. Although the two-dimensional inhomogeneity of the rolled MMCs did not have an effect on the precipitation sequence, the three-dimensional inhomogeneity of the HIPped materials did. During DSC experiments the temperature at which the $\theta'$ phase precipitated was a function of the matrix:reinforcement particle size ratio, and hence the dispersion of the reinforcement within the matrix. As the microstructure of the materials became more homogeneous, the precipitation of the $\theta'$ phase was at lower temperatures and thus ageing due to $\theta'$ precipitation was accelerated.

14. The variation in microstructural homogeneity in three dimensions was of a scale which did not affect the tensile properties of the rolled MMCs in either unnotched or notched specimens, despite extensive segregation of the reinforcement in two dimensions in some of the materials. The major influence on the tensile properties came only from the absolute size of the reinforcing particles.
15. Examination of the fracture surfaces has indicated that the spatial distribution of the reinforcement gives rise to localised variations in the failure mechanism of the materials of this study. This observation, together with the occurrence of multiple cracking during the tensile testing of the MMCs with the largest matrix:reinforcement particle size ratios, and the effect of the spatial distribution on edge cracking of the MMCs during rolling, implies that the level of microstructural homogeneity affects the fracture properties of the MMCs.

16. The results of notched tensile tests have shown that the best indicator of notch sensitivity is the ratio of notched UTS to unnotched yield strength. A trend of rising notch sensitivity (diminishing toughness) with decreasing matrix:reinforcement particle size ratio (decreasing segregation of the reinforcement) was observed. A possible reinforcement particle size effect, however, puts the validity of this observation into doubt. A more rigorous investigation of the effects of the microstructure of discontinuously reinforced MMCs on their fracture properties should be sought.

17. It has been shown that ease of processing of PM route discontinuously reinforced MMCs requires that the ratio of the matrix powder size to the reinforcement particle size should be as close to unity as possible. Current technology in bulk aluminium powder production limits the minimum average mass median powder size to approximately 15\(\mu\)m. If MMCs are to be produced without classification of the powder batches leaving large amounts of waste coarse powder, then a minimum reinforcement particle size of 15\(\mu\)m is required for ease of processing. It has also been shown that the tensile properties of the MMCs are maximised when the smallest reinforcing particles possible are used (much of current commercial MMC production by PM routes incorporates 3\(\mu\)m SiC\(_p\)). There is therefore a trade-off between cost, ease of production, and mechanical performance of MMCs produced via a PM route. For example, if reinforcing particles of 3\(\mu\)m in size are required for good mechanical properties, then ease of processing requires a very fine
average matrix powder size which can only be achieved by sieving of batches of powder and discarding the coarse size fraction which incurs a severe cost penalty.

10.2. Suggestions for Further Work

1. The results of this thesis have shown that the spatial distribution of discontinuous reinforcements has some effect on the processing and properties of MMCs. It has also shown the necessity for the characterisation of such spatial distributions in three dimensions. This would involve either imaging of the microstructure in the bulk of the material, or non destructive sampling of small very volumes of material for a technique based on local chemical analysis. It is unlikely that the latter can be achieved with current analytical techniques.

Three dimensional imaging of microstructures can potentially be carried out using confocal laser scanning microscopy (CLSM). This form of microscopy allows three-dimensional imaging to a depth of ~60μm only, and can only form images from materials which show low absorption of laser light. Both of these factors limit the use of CLSM for the three-dimensional imaging of MMCs.

X-ray microtomography (XMT) shows great potential for the purpose of three dimensional imaging. This allows the imaging of slices of the material without the need for physical sectioning of a sample. The slices are typically 10μm thick and the technique has a resolution of 15-30μm. This technique has already been used to assess large scale damage in SiC$_p$ MMCs [Mummery et al, 1993]. Unfortunately the X-ray linear absorption coefficients of Aluminium and SiC are similar which makes imaging of the microstructures of MMCs similar to those in this study difficult. XMT could be very useful however for many other materials. It is proposed that model systems which are ideal for XMT are studied first to assess the suitability and limitations of the technique.
for the purpose of microstructural imaging in MMCs.

Once three-dimensional images of microstructures have been obtained methods of taking measurements from them should be sought. This could take the form of developing computer software for the construction of three-dimensional Dirichlet tessellations for example.

2. The effect of the reinforcement on the precipitation behaviour of the matrix of the MMCs should be confirmed by the use of TEM. Dislocation densities after the solution treatment should be measured as a function of distance from the reinforcing particles into prior matrix particles. The volume fraction of the $\theta'$ precipitates should then be measured after isothermal ageing for various times, again as a function of distance from the reinforcing particles into the prior matrix particles. The volume fractions should be compared to that of the precipitate in the unreinforced alloy. In this way the proposal that clustering of the reinforcement affects the proportion of the matrix which exhibits altered ageing behaviour could be assessed.

3. It was indicated in section §2.5.5 that the wear properties of discontinuously reinforced MMCs may be partially dependent upon the quality of the dispersion of the reinforcement. Since wear is largely a surface engineering property it will be dependent upon the two-dimensional spatial distribution of the reinforcement. The MMCs of this study exhibited a large variation in microstructural homogeneity in two dimensions, but little variation in three dimensions. The wear behaviour of these composites may therefore be affected more by the spatial distribution of the reinforcement than the mechanical properties investigated here.
References


Antipas G., PhD in progress, University of Surrey, 1994.


Bader M.G., Private Communication, 1990.


Chapter 11. References


Chapter 11. References


Chapter 11. References


Lord Rayleigh, *Phil. Mag.*, 34, pp.481-507, 1892.


Chapter 11. References


Raghunathan N., Ioanidis E.K., Sheppard T., Accepted for publication in *J. Mats. Sci.* (Ref. KW/JM/89766).


Shakesheff b A.J., Defence Research Agency Report DRA/MS/TR93078/1, 1993


APPENDIX 1.

The Determination of Minimum Blending Time

To ensure that large scale variations in the spatial distribution of the reinforcement in the MMCs were not caused by poor blending of the two constituents it was important to determine the minimum time required to fully mix the matrix alloy powder with the reinforcing particles.

A sample of 480 g of Al alloy or copper powder was placed in a glass jar. A sample of 120 g of reinforcing particles was then placed on top of the matrix alloy powder. The glass jar was then sealed and placed into the Turbula T2C blender taking care not to allow mixing of the two components. The blender was then started so as to mix the blends. Periodically the blender was stopped and small samples taken from the top of the mixture for Malvern particle size analysis. It would be expected that as mixing progressed the mass median particle size of the samples should increase from the particle size of the reinforcement towards an equilibrium value when the blend would be thoroughly mixed. This process was then repeated for a number of blends containing differently sized matrix alloy powder and reinforcement.

A progression of four particle size distributions (after 5 min, 10 min, 30 min, and 60 min of blending) of one such blend is shown in figure A1.1. The particle size distribution for the mixtures is bimodal with one peak at small particle sizes attributable to the proportion of reinforcement in the samples, and a second peak at larger particle sizes attributable to the proportion of alloy matrix particles. After 5 minutes the mixture was still predominantly composed of reinforcing particles. After 10 minutes the proportion of matrix alloy particles had increased by a large amount. After 30 minutes the proportion of alloy matrix particles had increased a small amount more. After another 30 minutes the particle size distribution appeared not to have further altered indicating that the equilibrium size distribution had been reached and thus mixing was complete. A plot of mass median particle size against blending time is given in figure A1.2 for a number of blends tested in this way. It can
be seen from figure A1.2 that all of the blends appear to have reached equilibrium after 30 minutes of blending. It was decided that a safety margin should be incorporated into the blending to ensure thorough mixing so all blends for the production of MMCs were subsequently mixed for 60 minutes.

**Figure A1.1.** A progression of particle size distributions for samples taken at various stages of blending 54μm Al powder with 3μm SiC<sub>p</sub>. (a) after 5mins. (b) after 10mins. (c) after 30mins. (d) after 60mins.
Figure A1.2. Plot of mass median particle size of a sample taken from the top of a blend against the blending time after which the sample is taken.
APPENDIX 2.


This program is written in "Turbo BASIC" and then compiled to an executable file.

```
10 REM *** DIRICH4.BAS ***
20 SCREEN 2
30 CLS
40 DIM Y (1000)
50 DIM X (1000)
60 DIM RADI (1000)
70 RANDOMIZE TIMER
80 LET ARTOT=0
90 LET A=1
100 X (A) = (RND*610)+10
110 Y (A) = (RND*170)+10
120 RADI (A) = (RND*4)+2
130 FOR T = 1 TO A-1
140 H = X (A) - X (T)
150 H = H*H
160 J = Y (A) - Y (T)
170 J = J*J
180 DIST = (H+J)*.5
190 IF DIST < (RADI (A) + RADI (T)) THEN GOTO 100
200 NEXT T
210 CIRCLE ( X (A), Y (A), RADI (A))
220 ARTOT = ARTOT+(3.14*(RADI (A))
230 IF ARTOT > 18666 THEN GOTO 260
240 A = A+1
250 GOTO 100
260 PRINT A
270 DO UNTIL INKEY$ = "z"
280 LOOP
290 REM
300 REM *** dirichlet tessellation ***
310 REM
320 REM
330 DIM 1 (3)
340 DIM J (3)
350 Z = (640/200)*(3/4)
360 FOR Q = 0 TO 189
370 FOR P = 0 TO 629
380 FOR S = 1 TO 3
390 IF S = 1 THEN G=P
400 IF S = 1 THEN H=Q
410 IF S = 2 THEN G=P+1
420 IF S = 2 THEN H=Q
430 IF S = 3 THEN G=P
440 IF S = 3 THEN H=Q+1
```

Part one of program draws randomly generated particles.

Choose graphics screen.

Sets up arrays for X and Y positions of particles and their radii.

Initialises random number generator.

Initialises variable for total area of particles.

Initialises variable for number of particles.

Generates random position of particles and random radius between 2 and 6 pixels.

Checks to see if new particle overlaps any existing particles by comparing the distance between particles with the sum of their radii for all particles.

Draws circle for new particle.

Adds area of new particle to total area of particles.

Checks to see if total area allowed is not exceeded.

Adds 1 to total number of particles.

Prints total number of particles and waits until "z" key is pressed before continuing.

Section two of program constructs the Dirichlet tessellation around the randomly generated distribution of simulated particles.

The construction of dirichlet tessellations by the computer cannot be done in the same way as the manual construction. Here each pixel on the screen is considered in turn. The particle closest to the first pixel is found. If the particle closest to the pixel to the right of the first pixel is the same as that closest to the first pixel then the first pixel is ignored. If the two adjacent pixels have different closest particles then the two pixels are plotted on the screen. This process is repeated for the pixel below the first pixel to take account of horizontal lines.

- 245 -
DIST = 1000
FOR T = 1 TO A
R = ((X(T)-G)^2+(Y(T)-H)*Z)^2)^.5
IF R < DIST THEN I(S) = X(T)
IF R < DIST THEN J(S) = Y(T)
IF R < DIST THEN DIST = R
NEXT T
NEXT S
IF I(1) <> I(2) OR J(1) <> J(2)
THEN PSET(P,Q)
IF I(1) <> I(2) OR J(1) <> J(2)
THEN PSET(P+1,Q)
IF I(1) <> I(3) OR J(1) <> J(3)
THEN PSET(P,Q+1)
IF I(1) <> I(3) OR J(1) <> J(3)
THEN PSET(P,Q)
NEXT P
NEXT Q
OPEN "A:\RUNDATA" FOR OUTPUT AS #1
FOR K = 1 TO 189
FOR L = 1 TO 639
IF POINT(L,K) = 1 THEN WRITE#1,L,K
NEXT L
NEXT K
PRINT "COMPLETED"
DO UNTIL INKEYS = "z"
LOOP

This section stores the final screen once the tessellation has
been completed, by storing the horizontal and vertical
positions of the white points.

Signals the completion of the construction and storage of
data points, then waits until the "z" key is pressed.
Appendices

APPENDIX 3.

Computer Program to Illustrate the Local EDX Technique for the Characterisation of the Homogeneity of the Spatial Distribution of Reinforcing Particles

This program is written in Turbo BASIC and then compiled to an executable file.

```
10 REM ••• DOTS$4 •••
20 REM ••• INITIAL SETTINGS •••
30 RANDOMIZE TIMER
40 DIM X%(180,180)
50 DIM Z(1000)
60 SCREEN 1,0
70 CLS

80 INPUT "RANDOM DISPERSION OR CLUSTERS (R/C) "; DISP$
90 INPUT "OVERALL DOT DENSITY "; DOT
100 IF DISP$ = "R" OR DISP$ = "r" THEN GOTO 130
110 INPUT "ASPECT RATIO OF CLUSTERS "; ASP
120 INPUT "SHORT LENGTH OF CLUSTER "; SHORT
130 INPUT "SIZE OF MEASURING BOX "; BOX
140 INPUT "NUMBER OF MEASUREMENTS "; MEAS

150 NUM = (180^2)*DOT/100
160 IF DISP$ = "R" OR DISP$ = "r" THEN GOTO 1050
170 F = 180/(SHORT^2)
180 G = 180/(ASP*SHORT^2)
190 CLUST = PG
200 DENS = NUM/CLUST

210 XWHOLE = INT (180/(SHORT^2))
220 YWHOLE = INT (180/(ASP*SHORT^2))
230 XLEFT = 180-(SHORT^2*XWHOLE)
240 YLEFT = 180-(ASP*SHORT^2*YWHOLE)
250 IF XLEFT >= SHORT THEN XEDGE = SHORT ELSE XEDGE = XLEFT
260 IF YLEFT >= ASP*SHORT THEN YEDGE = ASP*SHORT ELSE YEDGE = YLEFT
270 RIGHT = INT ((XEDGE*ASP*SHORT*DENS)/(ASP*SHORT*SHORT))
280 BOTTOM = INT ((YEDGE*SHORT*DENS)/(ASP*SHORT*SHORT))
290 CORNER = INT ((YEDGE*XEDGE*DENS)/(ASP*SHORT*SHORT))
```
This section sets up and displays a clustered array of dots. Firstly, the complete array of pixel positions has a zero value assigned to it indicating that all of the pixels in the array are turned off.

If a random dispersion was chosen by the user then the program is diverted to a routine which displays a random dispersion.

For each of the whole clusters within the array the correct number of points are randomly chosen, and the corresponding pixels are turned on. If a chosen point is already turned on then another point is chosen. This ensures that the correct number of dots appear within the clusters.

If part clusters need to be displayed at the right hand edge, the bottom, and/or the bottom right hand corner of the array then the program is diverted to subroutines which set up and display them.

Once the array of dots is displayed the program waits until the user presses the space bar of the keyboard.

This section of the program takes measurements. Initially the pixels within the measuring box are all assumed to be off.

A random position for the measuring box is generated and the appropriately sized measuring box is drawn. The program then checks to see if each pixel within the measuring box is turned on or off. If the pixel is turned on then the corresponding value in the Z array is incremented by 1. This is repeated for the number of measurements chosen by the user.

Once the measurements are completed the program waits until the space bar is pressed. The display is then cleared.

The mean number of dots (pixels) within measuring boxes is calculated.

The standard deviation of the number of dots (pixels) within measuring boxes is calculated.
The coefficient of variation is calculated from the mean and standard deviation.

The user is asked if a hard copy of the results is required. If the reply is negative then printing of the results is bypassed.

The conditions set by the user at the beginning of the program are printed first.

The mean, standard deviation and coefficient of variation of number of dots within measuring boxes are then printed.

The user is now asked if the simulation should be repeated with the same parameters as the previous run. If so then the program is diverted back to the procedure for setting up and displaying the array of dots. If not then the user is asked if the simulation should be repeated with new parameters. If this is required then the program is diverted back to the point at which the computer asks for the operating parameters. If this is also not required then the computer asks the user to press the "Esc" key and the program is terminated.

This routine sets up and displays a random dispersion of dots (white pixels) within a 180x180 pixel area. Firstly a box is drawn delimiting the area of the dispersion. The horizontal and vertical positions of a point within the area of the dispersion are randomly generated. The computer then checks whether there is already a white pixel at this position. If one already exists then another random point is chosen; if not then the pixel at this position is turned on. When the total number of points are chosen and displayed the computer waits until a key is pressed before returning to the section of the program which takes the measurements.

This subroutine sets up and displays the part clusters which might exist at the right hand edge of the array of clusters. For each of these part clusters the appropriate number of points are randomly chosen and displayed within the clusters. After each point is randomly generated the program checks whether a pixel is already displayed there. If so a new position is generated and rechecked.
This subroutine sets up and displays the part clusters which might exist at the bottom of the array of clusters. For each of these part clusters the appropriate number of points are randomly chosen and displayed within the clusters. After each point is randomly generated the program checks whether a pixel is already displayed there. If so a new position is generated and rechecked.

This subroutine sets up and displays the part cluster which might exist at the bottom right hand edge of the array of clusters. For this part cluster the appropriate number of points are randomly chosen and displayed within the clusters. After each point is randomly generated the program checks whether a pixel is already displayed there. If so a new position is generated and rechecked.
APPENDIX 4.

The Characterisation of Inclusions

During the course of this study a small number of inclusions were identified in the MMCs. The elements detected by EDX analysis in these inclusions are shown in table A4.1.

<table>
<thead>
<tr>
<th>Inclusion Type No.</th>
<th>Elements Detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al, Si, Ti, V, Fe, Zr, Cr, Ni</td>
</tr>
<tr>
<td>2</td>
<td>Al, Fe, Cr, Cu</td>
</tr>
</tbody>
</table>

Inclusions of type 1 had the appearance of SiC reinforcing particles in the reflected light microscope, but were brighter than SiC particles in the SEM. These inclusions appeared in all of the MMCs, but were not present in the unreinforced alloys. This indicates that they arose from the SiC particulate raw material and could not be separated from the SiC particles.

A reflected light micrograph of the second type of inclusion is shown in figure A4.1. These inclusions had a central core with an outer zone. The interface between the core and outer zone was well defined, whereas that between the outer zone and the matrix was rougher and more diffuse. This indicates that the outer zone may have been due to a reaction between the core of the inclusion and the matrix of the MMC. EDX analysis of these inclusions was done to confirm this. Figure A4.2 shows a digital grey image of one of these inclusions. This reveals that the outer zone of the inclusion was in fact composed of two regions. Figure A4.3 shows the digital X-ray maps of Al, Cu, Fe and Cr for the same inclusion as that in figure A4.2. The region
of material surrounding the inclusion showed a matrix rich in aluminium with a small amount of copper, which contained sharply delineated areas which contained none of the elements mapped. This region was aluminium alloy matrix containing SiC particles. The core of the inclusion was rich in iron and chromium. The inner zone of the region surrounding the core of the inclusion contained aluminium, iron, chromium and a low concentration of copper. This suggests that this region is a reaction product between the Al-Cu alloy matrix and the core of the inclusion. The outer zone of the region surrounding the core of the inclusion also contained all four elements, but was rich in copper. This suggests that aluminium diffused from this outer zone into the inner zone to react with iron and copper which diffused from the core of the inclusion, whereas the tendency for copper to diffuse was much less.

This second type of inclusion was found in the first two materials produced and was thought to be caused by contamination from a sieve which was not perfectly clean even after thorough scrubbing. Subsequent materials were made from powders screened through a new sieve, and did not contain any of these inclusions. These inclusions were present in very small numbers, and since they were not present on the fracture surfaces of failed specimens it was concluded that tensile specimens did not fail prematurely because of their presence and that the mechanical properties of the materials were not adversely affected.
Figure A4.1. Reflected light micrograph of a typical type 2 inclusion.

Figure A4.2. SEM digital grey image of a typical type 2 inclusion.
Figure A4.3. Digital X-ray maps for the type 2 inclusion in figure A4.2. (a) Al map. (b) Cu map. (c) Fe map. (d) Cr map.
APPENDIX 5.

Publications

Details of publications based on material from this thesis are given below.


7. Stone I.C. and Tsakiropoulos P., "The Effect of the Spatial Distribution of Reinforcement on the Notched and Unnotched Room Temperature Tensile Properties of Al-4wt%Cu/SiC\textsubscript{p} MMCs", in preparation.
