Evolution of second phase particles with deformation in aluminium alloys

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Abstract

“Evolution of second phase particles with deformation in aluminium alloys” -
PhD thesis, Thomas Christopher Hill, School of Materials, University of
Manchester.

The effect of high temperature, high strain rate deformation on the evolution of
second phase particles in commercial aluminium alloys has been investigated. Three model alloys provided by Novelis have been examined, and the
evolution of particles during deformation has been examined for the alloy that
most closely resembles the composition of alloys used in commercial
applications. The effect of deformation mechanisms was expected to be an
enhancement of diffusion controlled processes; therefore the first part of the
work was to develop a heat treatment that would produce a fine distribution of
dispersoid particles. This heat treatment was then used to prepare material for
torsion testing, at strain rates similar to those found during the hot rolling stage
of commercial production. Testing was performed at both the end of heat
treatment temperature, to remove thermal effects, and at a lower temperature
which more closely represents the temperature during commercial rolling.
Material was examined by optical microscopy, FEGSEM and TEM and the
particle populations were characterised by backscattered FEGSEM imaging and
image analysis. This demonstrated that the dispersoid particle population
develops in multiple ways. Along with the enhancement of coarsening there is
a significant shape change to the dispersoid particles, suggesting a change in
the character of their interface. It has also been demonstrated that there is
nucleation of new particles, despite a long prior hold time, in material
deformed at the same temperature as the heat treatment. Material deformed at
lower temperatures also demonstrated a larger increase in the volume fraction
of dispersoid than material with the same thermal history. A constitutive model
for diffusion enhancement and a model for particle evolution have been
combined to simulate the effects of thermomechanical processing on the particle
population.
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Chapter 1 - Introduction

In order to place the research presented in this thesis into the context of the aluminium industry, this chapter presents an outline of the work involved in the commercial production of wrought aluminium alloys, from extraction to final product, and describes how the work conducted aimed to improve the process.

1.1 Outline

The work described in this thesis was part of a project proposed by Novelis Inc, intended to improve the mechanistic understanding of the wrought aluminium production process and the influences on microstructure and material properties. The project as a whole intended to eventually create a validated through process model of wrought aluminium products such as foil and can stock. The project would first break down the process into separate stages, corresponding to production processes; these would be examined in detail before the developed understanding could be combined into a full model.

The work presented here focussed on the role of high temperature deformation on the development and evolution of the dispersoid particles during the hot rolling phase of production. The project aimed to:

- Analyse the response of the supplied materials to heat treatments, aiming to find a heat treatment that produces a fine population of dispersoids suitable for further experimental work
- Analyse the effect of high temperature, high strain rate deformation, similar to the industrial hot rolling process
- Develop a model which can simulate the effects of the hot rolling process on the particle population, with the outlook towards being further developed into a through process model
To achieve this Novelis provided three model alloys, similar to those used in commercial applications such as packaging. The response of these alloys to heat treatment was evaluated by subjecting small samples to various isothermal treatments, and examining the resulting microstructure via microscopy. Following this ramped and isothermal heat treatments were employed, while conductivity measurements were used to assess the level of alloying elements remaining in solution.

Several options for achieving the strain rates that occur during commercial mechanical processing were considered, including performing hot rolling on a smaller scale. The final choice of deformation method was to perform extended deformation tests on Sheffield University’s arbitrary strain path machine. This allowed material to be created which had a known and controlled thermomechanical history.

Dispersoid population statistics were collected via image analysis of multiple backscattered SEM images, with numerical processing to separate out the dispersoid population statistics. This data has been used to plot dispersoid population distributions of size and aspect ratio as histograms, along with analysing overall statistics such as area fraction and median size.

From this comparisons have been made between materials deformed at different strain rates, and between areas of single specimens subjected to different levels and rates of deformation. Deformation has also been conducted at temperatures lower than the end of heat treatment, this simulated conditions closer to those found in commercial processing.

Additionally a model based on the work of Militzer (Militzer et al. 1994) has been created which calculates the enhancement of diffusion during deformation. This has been combined with an adapted Kampman and Wagner
(KWN) particle development model to simulate particle development during thermo-mechanical processing.

The rest of this chapter describes the commercial production of wrought aluminium alloys, in order to contextualise the work.

1.2 Industrial sheet aluminium production

While only the homogenisation and hot rolling process was covered by the work presented here, the preceding and following process must be considered to understand the results on the final material, and therefore understand the importance of each processing step.

1.2.1 Aluminium extraction

The extraction of aluminium on a commercial scale is performed via electrolysis of aluminium salts. To obtain the aluminium salts first aluminium ore must be mined, and then refined via the Bayer process to form purified alumina (aluminium oxide). This process involves washing the bauxite in a hot solution of sodium hydroxide, which converts the aluminium in the bauxite into aluminium hydroxide. The aluminium hydroxide is soluble in the solution allowing any insoluble impurities to be filtered out, and the purified alumina obtained via precipitation from the refined solution (Polmear I.J. 2006).

Once the alumina is obtained it can then be electrolysed to obtain aluminium. In order to do this it is first dissolved in molten Cryolite (Na$_3$AlF$_6$). This creates a solution which is both molten and electrically conductive, unlike alumina which remains solid over 2000°C and has low conductivity. This solution is contained within a reduction cell (Figure 1), which consists of a ceramic pot with a graphite cathode at the bottom, a baked carbon electrode which almost covers the cell, but leaves a small space for the gas to escape at the edges. This electrode forms the anode of the cell, and is consumed during the process as the oxygen from the alumina reacts with the carbon anode to form CO$_2$. The molten
aluminium is formed at the base of the cell; where it remains as it is denser than the molten salt mixture. The molten metal can then be drawn off once a sufficient amount has accumulated, and replacement alumina can be added. The carbon anodes are replaced periodically, as the consumption of these is preferable to the additional energy cost if an inert anode was used and pure oxygen was extracted at the anode. The cell is kept at the required temperature to keep the solution liquid by the resistive heating within the cell.

![Aluminium extraction cell](Polmear I.J. 2006)

As would be expected the energy cost associated with the extraction of aluminium during this process is still very high compared to that of other metals, the theoretical energy cost of extracting aluminium in this way is 6.34kWh/kg however in reality the commercial extraction process uses around 13KWh/kg. As the energy used in this process needs to be in the form of electricity, aluminium plants have historically been built close to sources of cheap electricity, such as hydroelectric or nuclear power stations.

In addition to the energy costs, aluminium production also has significant environmental impact. The energy production will always have some impact regardless of the electrical production method, and the process itself produces large amounts of CO₂, this is something that already has a non monetary cost
and may become financially costly in the future. However aluminium has a great advantage in that it is very easily recycled, and the recycling process is far less energy intensive than the extraction process.

1.2.2 Aluminium recycling
Aluminium recycling is a relatively simple process compared to its extraction from ore, the process requires cleaning or roasting the scrap to remove material that can cause impurities, and then remelting and refining the liquid aluminium. The pre melt cleaning processes usually involves shredding or crushing the scrap to the increase surface area and reduce the time needed for melting, followed by a high temperature drying (400°C), to remove oil and organic contaminants, or a very high temperature (500°C) delacquering treatment. Some scrap, such as cut offs from casting or other pre-use scrap, such as machining swarf may require little preparation before melting (Puga et al. 2009).

The total energy cost of refining and recasting scrap aluminium for use in place of fresh material is around 5% of the original extraction cost (Margolis 1997), this means that from an economic and environmental standpoint the use of recycled material is preferential for nearly all cases.

1.2.2.1 Limitations of recycling.
While recycling is preferable for the reasons previously detailed, the process is not perfect, material is lost over the stages of recycling, and the final product is not as pure as primary material extracted from ore (Bijlhouwer 2009). While novel methods for the recycling of aluminium have been able to recover a much larger proportion of material, they do not produce the initial material desired by the processing routes covered by this project, and are so irrelevant to this work.
While the recycling processes are designed to remove impurities from the material, there are some elements which tend to accumulate in the material and are not removed by the refining process. The most significant of these for rolled products is the accumulation of iron during the recycling and remelting phases of production, which can go on to have significant effects on the ultimate product.

Because of this in order to improve recycling rates it is necessary to understand the role these impurities will take during further processes and the effect these will have on the properties of the final product. This is the imperative for developing a deeper understanding of the complex processes that occur during aluminium production.
1.3 Industrial scale casting of aluminium

All aluminium products must go through some form of casting process during the production route. The casting process is usually the stage at which the material has any alloying elements added, and a final refining process is undergone before the material is solidified. In addition to alloying elements, grain refiners can be added in order to improve the cast microstructure of the material. For the production of aluminium sheet on a commercial scale, the material must be cast into large rectangular cross section billets, which will allow for the maximum utilisation of material during rolling. These billets are produced by direct chill (D.C.) casting. The advantage of D.C. casting compared to fixed mould casting is that the solidification process, and hence the properties of the solid, can be more finely controlled (Jarrett et al. 2011). A D.C. caster consists of a furnace in which metal is melted, refined and additions are made, a launder system, which transfers the liquid metal from the furnace, and a mould with a movable base in which material is cast and cooled. An illustration is given in Figure 2.

The first step in the casting process is to add material to the furnace; this will consist of the “pure” aluminium, along with the alloying additions, and the grain refiner if it is already included in an alloy. The furnace then heats and melts this material, which is then thoroughly mixed in order to distribute the additions throughout the material, the melt is then allowed to settle so that impurities can either sink to the bottom where they will remain, or rise to the top where they can be skimmed off. Inert gas is bubbled through the melt in order to remove other gasses which may be dissolved within the alloy.
The liquid metal is then poured into the launder system, which directs the material to the mould and filters out impurities such as oxides which could be detrimental to the strength of the cast material. The mould consists of a steel ring which determines the cross-section of the billet, with a steel base supported by a ram. The sides of the mould are water cooled. The material fills the mould, which solidifies along the mould walls first, then the base begins to be lowered and the material input is controlled so the level in the mould ring remains constant. This means the solidification of the material is both rapid and occurs under constant conditions, reducing segregation of material through the billet. Water also falls alongside the billet as it is lowered, extracting even more heat. The rapid cooling rates help reduce the grain size of the material compared to processes such as sand casting. However as cooling rates are high there can be variance in microstructure between the centre of the billet and the surface, where cooling rates are the highest (Eskin et al. 2004).

The billets produced by this method contain randomly orientated grains, consisting of a primary aluminium phase with eutectic second phase distributed both within and at the edges of grains. The grains tend to be
generally round with a dendritic structure within, made up of a single second phase. Due to the conditions of solidification (rapid solidification, good mixing of the melt and relatively fast cooling of the solid) the Schiel solidification model (D A Porter & Easterling 1996) is a close approximation to the casting process. This means that the phases likely to be present after this casting method can be easily calculated provided the composition is known. While second phase particles are formed, the primary aluminium phase is usually left supersaturated with the alloying elements due to the rapid cooling rates. The grains within the billet may vary in size and shape by reasonably large amounts, and the second phase structures are also reasonably large. The spacing of the primary dendrites tends to be larger towards the centre of the cast billet, and faster cooling speeds result in a finer grain size (Eskin et al. 2004).

*Figure 3 Typical as cast microstructure viewed under cross-polarised light (0.1% Mn as cast material)*

While the conditions of casting are controlled in order to improve the quality of the material produced, the material is not yet ready for rolling to thin sheet or foil, and must pass through more processing steps. Firstly the billet itself may
not be smooth and flat enough along the surface to be rolled, this is sometimes prevented by use of an electro magnetic field, but if present the surface irregularity can cause issues during rolling and so the billet must be mechanically smoothed. While the waste from this scalping procedure can be recycled, it is time consuming and creates an additional step in the production process.

Once the material is physically ready for rolling, the next step is to heat treat the material in order to prepare the material for deformation.

1.4 Homogenisation heat treatment

The pre deformation heat treatment has multiple objectives, firstly it aims to make the microstructure of the material as uniform as possible, by removing the microsegregation which occurs during casting by promoting diffusion and allowing the elements tend towards an equilibrium situation. Secondly it aims to remove phases which may be detrimental to further processing; these phases tend to be those which may act as nucleation sites for cracks during deformation processing. Finally it aims to nucleate and grow a dispersion of particles that will help control microstructural evolution during further processing. These requirements mean the heat treatment must be relatively long for the high temperatures used (+500°C), in order to allow for diffusion and nucleation within the material. It has also been found that higher temperature homogenisation treatments reduce the flow stress of the material, which is important for deformation modelling (Kubiak et al. 2010). Homogenisation has also been shown to improve the response to annealing after cold work in strip cast Al-Mn alloy (Birol 2009). During the work presented here the project developed a heat treatment to produce a dispersoid particle population suitable for experiments. In the industrial production process the heat treatment has several functions.
1.4.1 Removal of Micro segregation
Micro segregation occurs during material casting and is an unavoidable consequence of the nucleation and growth of a solid phase in a material. When the primary phase nucleates and grows the surrounding liquid is enriched in alloying elements in solution, until the liquid reaches the concentration and temperature reach the eutectic point and solidifies, this produces the dendritic structure seen within the as cast material (D A Porter & Easterling 1996). The high temperatures during homogenisation creates conditions under which diffusion can take place and these elements can diffuse back into the primary phase or to particles of new phases once they have been nucleated.

1.4.2 Removal of second phase
Due to the conditions under which solidification occurs there are often phases present in the cast material which are either unwanted or actively detrimental to the properties of the alloy. These form the eutectic network structure seen in the cast alloy; this tends to break up during the homogenisation process to form what are known as constituent particles. In the alloys considered in this work (3XXX series aluminium) these particles are of the incorrect phase for the desired effects to occur. As these phases are present in excess of equilibrium concentrations, the heat treatment allows some of the elements from the constituents back into solution or converts the phase to another more desirable form.

1.4.3 Precipitation of dispersoids
As constituent particles do not have the required properties for microstructural control, it is necessary to create fine “dispersoid” particles in the material. These are nucleated within the primary phase and the growth is controlled by the composition and process parameters (Kubiak et al. 2010), the exact heat treatment conditions are therefore selected to both nucleate and grow this desired phase. Multiple step heat treatments or slow heating rates can be used
in industry in order to obtain the ideal microstructure. The exact phases and elements relevant to this project are discussed in section 3.2. Dispersoid particle can be very fine, usually 20-200nm, and it may only be possible to view them by electron microscopy. These dispersoids have been shown to increase the strength of the material via dispersion hardening (Muggerud et al. 2013), but this is not their primary purpose in these alloys.

1.5 Hot rolling

Once the material is heat treated it is hot rolled. This reduces the thickness of the billet by several orders of magnitude, creating strip which is then collected on a roll. The hot rolling process is not one single reduction, but several passes through different stages of rolling. This working breaks up the grain structure present after casting. Firstly the grains become elongated in the rolling direction due to the deformation of the material, however the high temperatures mean that the material can recrystallize during this deformation and following heating cycles, forming smaller, randomly orientated and evenly sized grains (Zhang et al. 2001). This processing also helps distribute the particles present in the material more evenly, and breaks up the larger particles that persist after the homogenisation process from the original second phase.

The processing consist of several passes through a reversing set of rolls, known as a break down mill, in which the material is reduced in thickness from the billet width by around 90%. This is a large deformation and the strain rates during this stage of rolling can be very high, in the order of 100s⁻¹ (Novelis 2011). This is then followed by passes through further sets of rolls which determine the eventual strip thickness, which will be less than 10mm.

This process and any effects on the microstructure is the main focus of this project, specifically in examining the ways in which high temperature, high strain rate deformation changes the constituent and dispersoid particles within
the material. The high strain rate deformation causes a large increase in the dislocation density of a material, this leads to an increase in vacancy concentration. This could have a major effect on the diffusion and interface controlled processes within the material and is discussed further in section 3.5 regards to the evolution of specific particles.

After hot rolling the material is allowed to cool, during which time recovery and recrystalization continue (Naiyu Sun et al. 2006)(Suni et al. 1998), depending on the kinetics, the factors contributing to the increased diffusion may remain for some of this period.

![Figure 4 A hot rolling (breakdown) mill (redrawn from Callister 2007)](image)

It is this process that the work presented here has focussed on. Specifically the experimental work aimed to accurately replicate hot rolling conditions such as strain rate and temperature in a controlled manner, while modelling work aimed to simulate any observed effects

### 1.5.1 Warm Rolling

During the warm rolling stage of production the material is further reduced in thickness at a temperature of around 275°C, during which the material can be deformed more easily, but recrystalization will not occur. The rolling
equipment is similar to that used for hot rolling; however the rolls are smaller in diameter in order to cope with the thinner material, this means that the rolls are arranged in “clusters” so that they do not flex under the stress of rolling. This process gives a strong cube texture to the material due to the lack of recrystallization.

1.6 Annealing

Between the warm and cold rolling stages the material is annealed in order to control the amount of work hardening present in the final material, this also promotes recrystallization. This uses temperatures of around 350°C which allow dislocations and vacancies formed by the deformation during cold working to diffuse through the material and annihilate (Humphreys & Hatherly 2004), and triggers recrystallization at points with high stored energy. This also alters the texture of the material, as the recrystallized grains give the material a different texture; this is discussed in more detail in section 2.3

The annealing process reduces the strength of the material slightly (Gutierrez-Urrutia et al. 2005) (Gomaa et al. 2003), but the improvement in formability it produces is often critical for downstream processing, such as deep drawing. It is during this stage that the dispersoid particles are important, and so the ideal population of dispersoids should be present at this point, if required. Once annealed the material returns to the cold rolling mill for final reduction.

1.7 Cold rolling

Cold rolling is used to deform the material further and produce plate, sheet or foil depending on the thickness required. The process works in a similar way to the hot rolling process although the lower temperatures mean that the material is not able to recover fully and recrystallize and so strain hardening occurs (Mülders et al. 2002). There can be annealing stages in between passes in order to reduce this if large deformations are used, this stops fracture occurring due
to the build up of work hardening. This rolling process also promotes the development of a texture, as the grains are deformed heavily deformed and tend to become aligned due to the nature of the deformation (Liu & Morris 2003).

Figure 5 Cold rolling "cluster" mill (redrawn from Roberts 1978)
Chapter 2- Literature Review

The alloys being considered in this project are 3XXX series aluminium without magnesium content. These alloys are used for food packaging in the form of foil and thin sheet, and are chosen for their strength, formability and corrosion resistance (Polmear 2006). The main alloying element in these alloys is manganese, with some silicon and a very low level of titanium from grain refiner. However, as previously discussed there is also a level of iron present in the material, dependent on the amount of contamination from recycling. The concentration of each element present in the alloy determines the phases present both after solidification and during processing, and therefore the nature of the particles within the material.

The final properties of this material are a result of complex interaction between the two types of particle present, the underlying microstructure and the thermomechanical processing. This section of the review covers the literature relevant to the second phase particles present in these alloys.

2.1 Constituent particles

Constituent particles are large particles formed during the solidification of the material, and they continue developing during the production process.

2.1.1 Formation

The constituent particles originate during solidification of the alloy. According to established solidification theory, as the liquid metal is cooled below the melting point the undercooling creates a driving force for solidification, the alloy then begins to solidify heterogeneously on grain refining additions. As it solidifies it forms dendrites which grow into the surrounding liquid. The solid formed during this process contains a lower amount of the alloying elements, although due to the fast solidification rate there remains some supersaturation
of alloying elements. This is dependent on the rate of cooling, and in material from commercial DC casting the Mn supersaturation can be as high as 0.9wt\% when the total Mn concentration is 1wt\% (Tilak & Morris 1985). As the alloy has a higher than equilibrium concentration, while this process continues the alloying elements become more concentrated in the remaining liquid. Eventually this process reaches a point where the amount of solute in the remaining liquid reaches the concentration required to solidify as a eutectic or peritectic. When this happens the spaces between the dendrites are filled by the solidified eutectic structure of the aluminium and the second phase. This produces a network of second phase in the interdendritic spaces (Skjerpe 1987). While 2 dimensional micrographs suggest these are many individual particles, this structure is in fact a matrix of interconnected second phase (Dwyer et al. 2013).

The spacing of these particles, known as the “interdendritic spacing” is controlled by the cooling rate, and so the particles are closer together in the rapidly cooled edge material. (Li & Arnberg 2003). The exact phase that is formed during solidification is determined by the composition of the starting liquid (Meredith et al. 2002) (Eskin et al. 2004) however for the alloys examined in this work the phase formed is the Al₆(Mn,Fe) intermetallic. As the solubility of Fe within aluminium is very low the particles tend to contain most of the Fe, while Mn often remains in relatively high supersaturation within the matrix.

2.1.2 Development During heat treatment
The majority of evolution of the constituents happens during thermal processing of the material. Accordingly this is the area that previous research has most focussed on (Hamerton et al. 2000). There are several processes which occur during thermal treatment that control the development of these particles. Due to the nature of the phase it is not possible to completely dissolve the
second phase particles, therefore the material must be processed to utilise the constituent particles later on.

During heat treatment the interconnected network of particles is broken up, this occurs both to thermal stress and the process of spheroidization. The thermal stress occurs from the differing thermal expansion rates of the two phases present. As the material is heated this leads to stress across the network. This is concentrated where the section is smallest and eventually fracture occurs as seen in Figure 6. This results in many separate particles being formed. Experimental work has shown that this process is generally seen when the material is subjected to fast heating rates, such as when treated isothermally in a fluidised bath (Alexander & Greer 2005). However commercial heat treatments usually use a slow heating rate of around 50°/h so this is less important to industrial processing.

![Figure 6 Backscattered electron image of constituent particles, showing beak up and different phases (Alexander & Greer 2002)](image)

Spheroidization is the process by which a non-spherical particle will tend towards becoming spherical over time, this occurs due to the surface energy associated with the interface between the two phases. As a sphere has the lowest surface area to volume ratio of any shape, the particles will tend towards
spherical if possible in order to reduce the surface energy. However this process is controlled by the mobility of the interface, which is in turn controlled by the temperature. This results in much faster spheroidization at higher temperatures. These processes combine during homogenisation treatments to produce smaller rounder particles than the large, complicated structures seen after solidification.

Once the particles have formed they then undergo coarsening. This process is due to the associated surface energy of the interface between two phases. As a single large particle will have a smaller surface area than several single particles totalling the same volume of phase, a process by which this can happen is energetically favourable. This process occurs between all particles in a material, even if there are several varied populations present. Coarsening will remove the smallest particles present, eventually resulting in a single particle distribution (Brown 1989). As with nucleation, this process is often controlled by the properties of the particle interface (Ferrante & Doherty 1978). Rather than the second phase moving as one this process occurs via the diffusion of alloying elements from smaller particles to larger particles.

The diffusion is driven by the Gibbs-Thompson effect whereby solute will be more concentrated next to a particle with a small radius compared to one with a larger radius, creating a diffusion gradient. This is because a tighter curved surface has a higher free energy than a larger radius surface, meaning smaller particles are at equilibrium with the matrix at a higher bulk concentration of solute, however as the distances involved are large and the diffusion of some elements is slow, this process takes place only on large timescales for constituents. As diffusivity increases exponentially with temperature, thermal breakup is mainly seen during heating and at low temperatures, while coarsening is seen mainly in high temperature treatments (Li & Arnberg 2003).
Along with spheroidization and coarsening, the particles can be transformed from one phase to another. The phases formed during solidification are determined by the conditions at the time, however during the heat treatment there may be a different phase which is favoured. This is most often seen in Mn containing alloys as a transformation of the Al₆(Mn,Fe) phase to the α-Al-(Fe-Mn)-Si phase (Alexander & Greer 2002).

Work on roll bonded couples shows that the conversion of Al₆Mn phase into the new alpha phase is controlled by the diffusion of silicon into the pre-existing particles (Alexander & Greer 2004b). This is a eutectoid transformation and occurs rapidly once the new phase has nucleated within the pre-existing particles. The amount of transformation which occurs is limited by the availability of silicon from the surrounding matrix, and therefore on the original alloying level.

This work also showed that this transformation can enhance the breakup of large constituent particles. It was observed that in particles containing a “duplex” (α/Al₆Mn) boundary that the matrix will begin to wet this boundary, gradually growing into the gap, eventually resulting in two separate particles each of a single phase. This discovery suggests that this two phase boundary has a very high interfacial energy and so any interfaces which still remain after heat treatment are potential weak points during hot rolling, at which the particle will break. Particle transformation is shown in Figure 7.
It should also be noted that due to the supersaturation of alloying elements within the matrix, notably Fe and Mn, when held for long periods at high temperature, these alloying elements will make their way to the particles, increasing the volume fraction of the second phase, and increasing particle size past what would be expected from pure coarsening. However, this supersaturation is usually used to allow dispersoids to be precipitated.

### 2.2 Dispersoids

Dispersoids are very fine (<1 µm) second phase particles, usually formed during heat treatment processes. They are observed in many alloys in which there is a supersaturation of alloying elements present in a material, and are formed from deliberate alloying additions, as the dispersoids are used to control recrystallization.

The supersaturation of alloying elements in the material means that it is favourable for these elements to form a second phase within the alloy, rather than to remain in supersaturation (Lifshitz & Slyozov 1961). This driving force is strongest at low temperatures, however this process does not usually occur at
low temperatures as the mobility of the elements is very low due to the low
diffusion rates in these alloys. Therefore the alloy must be heat treated in order
to produce sufficient diffusion to allow nucleation and growth of particles.

Homogeneous nucleation of the dispersoid particles found in 3XXX series
alloys is very unlikely due to the high energy barrier for this to occur (Porter &
Easterling 1996). This energy barrier is due to the misfit between the matrix and
second phase, which means that there must be elastic some strain around the
particle as it forms to allow it to fit in the matrix. In addition an interface must
be created between the two phases. It is therefore assumed that dispersoids
must nucleate heterogeneously on an existing particle or flaw in the matrix. One
suggestion has been that dispersoids nucleate on very fine pre-existing
magnesium containing particles (Lodgaard & Ryum 2000). This has been
previously shown by (Alexander & Greer 2004a) in certain alloys. While this is
possible for some alloys that contain magnesium as an alloying addition, it is
not for those containing no magnesium. Therefore it must be the case that
dispersoid nucleation occurs on another form of site. Grain boundaries are
usually considered to be an excellent nucleation site, however in these alloys
grain boundaries are usually the site of constituents, and areas of grain
boundary without particles are likely to be depleted in solute due to the rapid
diffusion rate along grain boundaries. Despite this, sub grain boundaries
present a possible site for nucleation if these are present within the material.
Vacancies, specifically vacancy clusters could also act as nucleation sites, but
like sub grains sufficient availability of these sites is only present in material
which has been significantly deformed.

Dislocations therefore present the most likely possibility for nucleation sites in
these alloys. The distortion of the lattice around the dislocation creates a strain
field, which the nucleating particle can then utilise to reduce the strain field
created due to the mismatch in atomic spacing between the matrix and the new
phase (Cahn 1957) (Jena & Lahiri 1981). This reduces the energy barrier for the nucleation of a particle and the critical radius of particle needed for it to become established. While the dislocation density is increased by deformation (Arsenlis & Parks 1999), they are always present within crystalline materials to some extent, and so are present during homogenisation in order for precipitation to occur.

The formation and growth of these dispersoids has been widely examined in the literature. Some work has suggested that the particles form as a type of quasi-crystal to begin with, before transforming as elements diffuse into the particle (Hansen et al. 1989). This idea has generally been surpassed by other work which has suggested that the particles nucleate as the $\alpha$-Al(Mn,Fe)Si phase to begin with, but first form with coherent interfaces before becoming semi-coherent as their size increases. This is suggested from the strain fields and moiré fringes observed in TEM images of precipitated particles (Li et al. 2010) (Du et al. 2013).

A change between coherent and semi-coherent particle interfaces has been observed for other particles, and is considered to be size controlled rather than a change in the particle structure, as the misfit due to a small particle can be accommodated in all directions by dislocations, while above a certain size the misfit is too great for this to occur.

The usual $\alpha$-Al(Mn,Fe)Si phase that makes up dispersoids in these alloys has a simple cubic or bcc structure, and the exact chemical composition varies between particles. Orthorhombic Al₆Mn dispersoids can also be formed in commercial alloys (Meng & Northwood 1988). The dispersoids themselves usually take a plate or block like shape, and are in the order of 10-200nm in size depending on the conditions of formation (Li & Arnberg 2003). Depending on the composition of the alloy, other phases, such as the Al₆(Mn,Fe) phase that
makes up the post casting constituents may also form. This is dependent on the composition of the alloy, specifically the level of silicon available, along with temperature for nucleation.

Once grown, the particles are always semi-coherent, with only one surface coherent in one dimension with the matrix. This is due to the similarity of lattice spacing in this direction. This gives the particles their non-spherical shape, as the growth of the coherent interface requires far less energy than growth of the incoherent interface. The coherent interface is also less mobile than the incoherent interface, further promoting growth by the incoherent interface. This results in elongated “plate-like” particles with a large coherent interface and a small incoherent interface as seen in Figure 9.
It is this low surface energy which allows a high density of dispersoids to be precipitated, as the nucleation barrier is relatively low as long as sufficient dislocations are present. There is a relatively low driving force for coarsening between the particles compared to if the surfaces were incoherent with a large surface energy, so the particles do not rapidly coarsen once nucleated.

Li and Arnberg have extensively examined the nucleation and growth of dispersoids during heat treatment (Li & Arnberg 2003). This work has demonstrated that at lower temperatures during heating, nucleation of dispersoids occurs first in the areas with the highest supersaturation of Mn, therefore in the areas furthest from the constituent particles. Additionally it was shown that the density of dispersoids reaches a maximum during heating at around 400°C before being reduced due to dissolution and coarsening, while the size continues to increase until around 530°C, above which particles are dissolved. This agrees with other experimental work on the evolution of particles during heat treatment where dispersoid precipitation was found to occur from 350°C and dissolution occurred above 500°C (Dehmas et al. 2005).
Investigations have also shown that the Mn/Fe ratio within the dispersoids changes with increasing temperature, with particles formed at lower temperatures having far higher Mn/Fe ratio than those at higher temperature. It was suggested that this is due to adsorption of the Mn by the primary particles, although a simpler explanation may be that Fe is far less likely to go back into solution than manganese due to its low solubility.

Most experimental work carried out has only examined a ramp and hold heat treatments, which is unlike that used in industry which use a ramp followed by a temperature drop. Some work has looked at these forms of treatments, but they did not examine the change to dispersoids in great detail (Pettersen et al. 2002)(Huang & Ou 2009)

Further extensive work using TEM has demonstrated that the dispersoid particles have a particular alignment with the matrix due to the coherent interface. To minimise energy the coherent face lies on the {111} (close packed) planes of the Al matrix. (Li et al. 2012) this is shown in Figure 9.

Additionally, experiments have shown that the precipitation of dispersoids can be increased when the material is deformed before heat treatment; this is due to both the increased presence of dislocations, which create more opportunities for precipitation to occur, along with microsegregation of the solute increasing the localised concentration. (Chen et al. 2003) This effect will be discussed further in section 3.4.

Once nucleated, the dispersoids grow via the diffusion of supersaturated elements from the surrounding matrix to the particles. This continues until the supersaturation of the limiting element (usually manganese) has been removed. At this point the density of dispersoids is highest, and the volume fraction has also reached its maximum. At this point the dispersoid population should fit the predictions of LSW theory, with a negatively skewed distribution. As the
population coarsens this would be expected to shift towards larger sizes, however the distribution may change due to the complex interactions between matrix, constituents and dispersoids (Brown 1989). In general the dispersoids produced at temperatures of 500-600°C in commercial alloys have been found to fall into the size range of 20-80nm for the peak of the population curve (Figure 10).

Figure 10 Size distributions of dispersoids after heating to different temperatures in AA3003 (Y. J. Li & Arnberg 2003)

From this point the evolution of dispersoids is controlled by coarsening. This occurs more rapidly for the dispersoids than constituents as they are much closer together, and therefore the distance for atoms to diffuse is reduced and the time taken is inversely proportional to the square of the distance. As it is the slowest diffusing species in these alloys, manganese is likely to be the limiting factor in this process. Coarsening of this type of particle was observed during a hold at 600°C by Li, shown in Figure 11.
As with the constituents, larger particles grow at the expense of the smallest, leading to a reduction in particle density and an increase in mean size, however this process occurs between all of the particles, both constituents and dispersoids, in the material. Therefore if the temperature is held for a long period, dispersoids close to constituents will reduce in size and eventually dissolve, while those out of range will coarsen between themselves. If this process is allowed to continue for long enough all of the dispersoids will be completely removed as the constituent particles grow, slowly expanding the precipitate free zone (PFZ) outwards. Micrographs demonstrating this are shown in Figure 12.
This process is enhanced by the conversion of the constituents creating a compositional gradient of Mn (Dehmas et al. 2012). For this reason, heat treatments aiming to produce a fine dispersoid population are usually as short as possible to create a relatively even distribution throughout the material. Therefore commercial heat treatments may consist of the 50°C/h ramp to around 600°C, acting to allow diffusion of the solute elements, before the temperature is dropped to promote nucleation and growth of the dispersoids.
2.3 The roles of second phase particles during deformation processing

Constituent and dispersoid particles take opposing roles during and after the deformation of the material. It is well understood that the presence of non deformable particles above a certain size threshold in an aluminium alloy will act as nucleation sites for recrystallization after deformation (Humphreys 1977), with a particle size of 1-2µm needed for nucleation in a highly deformed material, and larger particles needed if the strain is lower. This is due to the localised deformation of the material around the particles, caused by the rotation of the matrix next to the particle; this can be observed in these alloys after hot rolling, and is more pronounced around plate like constituents (Liu et al. 2009). Conversely smaller particles are known to restrict the growth of new grains during recrystalization, by pinning the grain boundaries of new grains due to the Zener pinning effect. The constituents in the alloys considered for this work are usually large enough for particle stimulated nucleation (PSN) to occur, although some are too small.

During the hot rolling, the material will usually recover and recrystallize regardless of particles due to the high temperatures and strains involved. It is later on, during the annealing process that concentrated deformation around constituents and the associated stored energy can again trigger recrystalization. These particles reduce both the necessary annealing time and the resulting grain size (Humphreys & Hatherly 2004) this improves the materials properties, especially formability. However grains formed due to PSN will produce a random texture to the material, while grains that grow from existing deformed grains will have a cube texture; this has an important effect on further processes.

The texture of a material describes the orientation of the grains in general. A material with a strong texture will have most grains orientated in the same way,
while a material with a weak or random texture will not. Texture has a strong effect on the formability of a material, in the deep drawing process used for can manufacturing strong textures lead to earring of the material at the top of the pressing, shown in Figure 13. Different textures produce different kinds of earring, shown in Table 1.

![Figure 13 Earring after drawing process](image)

(a) material with a mixed rolling and cube texture, (b) material with a strong cube texture (Humphreys & Hatherly 2004)

<table>
<thead>
<tr>
<th>Texture</th>
<th>Name</th>
<th>Earing</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100] &lt;001&gt;</td>
<td>Cube</td>
<td>4 fold 0/90° etc</td>
</tr>
<tr>
<td>[110] &lt;001&gt;</td>
<td>Goss</td>
<td>2 fold 0/180°</td>
</tr>
<tr>
<td>[110] &lt;112&gt;</td>
<td>Brass</td>
<td>4 fold 45° etc</td>
</tr>
<tr>
<td>[112] &lt;111&gt;</td>
<td>Copper</td>
<td>4 fold 45° etc</td>
</tr>
<tr>
<td>[123] &lt;412&gt;</td>
<td>S</td>
<td>4 fold 45° etc</td>
</tr>
</tbody>
</table>

Table 1 Textures and associated earring after drawing (Humphreys & Hatherly 2004)
Ideally no earring is desirable, as it results in waste material when cut off, to achieve this it is therefore desirable to have a balance of textures in the final, pre-drawing material. To achieve this the material must have a balance between the textures that will be formed during cold rolling (Brass, Copper ,S), and the Cube texture. This is achieved by retaining a strong a cube texture after the annealing stage, rather than allowing the random PSN texture to dominate.

The inhibition of recrystallized grain growth, and thus the retention of the desired texture, comes from the dispersoid population. The dispersoids are all far too small for PSN to occur and so always act Zener pinning sites, restricting the growth of new grains. Zener pinning is the effect of small particles in inhibiting the motion of a grain boundary. This is because having the particle on the grain boundary reduces the grain boundary’s energy by reducing its area. This counteracts the growth of new grains during recrystallization, as nucleated grains grow by the movement of a grain boundary through the deformed material. By stopping this the effect of Zener pinning is to limit the amount of recrystallized growth that occurs (Nes 1976)(Nes et al. 1985). A higher density of dispersoids will reduce the size of recrystallized gains and increase the time taken for recrystalization to occur (Suni et al. 1998). This effect has been observed in similar alloys that contain Al₂Mn precipitates, in a proportion similar to that expected for the α-phase dispersoids in the alloys examined here. (Rios 2004). Other work on dispersoid containing alloys has shown that the presence of dispersoids inhibits the formation of dislocation “walls” and cells, and a more homogeneous form of deformation occurs (Apps et al. 2005). This may also account for a reduction in the recrystalization, as there will be fewer areas of concentrated deformation.

The Zener pinning potential of the dispersoids is determined by several factors. Smaller particles will have a stronger Zener pinning effect, or equivalently a higher number density of particles will also have a stronger effect for a given
volume fraction of dispersoids. Therefore the strength of the pinning pressure is essentially reduced by coarsening of the dispersoids. Another control on the amount of Zener pinning comes from the shape of the particles (Li & Easterling 1990). While the original calculation of pinning potential concentrated on the effect of spherical particles, this work calculated how an ellipsoid particle would control boundary movement, showing that if orientated in the plane of the boundary there will be a higher pinning pressure, especially if the particle is coherent. However this is very dependent on the orientation, and with only a small change the effect drops off. This may be an important effect in the alloys discussed here due to their tendency to have a particular alignment within the matrix.

This interaction between the counteracting PSN and Zener pinning effects controls the growth of grains, and consequently the texture during annealing and at the end of processing. If no dispersoids are present then the level of recrystallization nucleated at particles will be very high, therefore the material will develop a relatively strong rolling texture after final rolling. Opposing this if the dispersoid population is such that the Zener pinning effect is very strong then there will be too little random recrystallization and the cube texture will be retained. What is usually required is a balance between these two textures, which will result in little earring during a deep drawing process and a good formability in foil products.

The deep drawing process is also improved by the transformed constituent α-particles within the material, which due to their hardness act to clean the dies of the drawing equipment of any aluminium build up.
2.5 Deformation mechanisms

2.5.1 Dislocation Theory

The strength of crystalline materials such as aluminium is far lower than would be expected from a simple calculation taking into account the strength of the atomic bonds, therefore some form of flaw in the crystal structure must allow deformation to take place. These flaws are called dislocations, and were first proposed long before they could be directly imaged (Hull & Bacon 1984).

A dislocation is a flaw in the crystal lattice, two kinds of dislocations can be considered, “edge” and “screw” types. An edge dislocation can be considered to be caused by an extra half plane of atoms in the matrix, the edge of which is the centre of the dislocation, to move through the material the half plane joins with part of a neighbouring plane, the other part becoming a half plane instead. This allows part of the material to move one atomic space across, without having to break all the atomic bonds in the plane perpendicular to the additional half plane. Screw dislocations are harder to visualise but they consist of a split in a lattice plane which joins down to the next plane, and so on such that a path around the end of the split would take a spiral path down through each layer.

A dislocation can be defined by its “Burgers vector” the vector of the displacement to the matrix around the dislocation. For a perfect dislocation this must be a lattice vector to ensure the perfect crystal structure is restored after the passage of the dislocation. The dislocation line is another important characteristic and is the line around which the distortion occurs. A line dislocation has a Burgers vector perpendicular to the dislocation line, whereas in a screw dislocation they are parallel.
In reality dislocations in real materials usually have both screw and edge components, as such they can be considered as lines through the material around which there is a concentration in the deformation of the lattice.

Dislocations are mobile and move when the material is deformed, they can also curve, and change from edge to screw type, but to remain mobile they must usually remain in one plane of the lattice.

Additionally dislocations can separate out into what are known as partial dislocations, these take the form of two separate defects, the combined Burgers vector of which is equal to that of the original dislocation (Bogers & Burgers 1964). Partial dislocations are formed if they have a lower combined energy than that of the original dislocation, in an FCC material the energy of a pair of partial dislocations is determined by the stacking fault energy. Partial dislocations can be mobile (glissile) where the Burgers vector remains in the plane of movement, or fixed ( sessile) where the Burgers vector is no longer in the plane of the dislocations movement.

As all dislocations are defects within the crystal, they are always surrounded by a strain field of distorted lattice; dislocations will have different stain fields depending on their characteristics.

If dislocations meet they interact due to the strain field around their cores. Dislocations may collide and pin each other in place, otherwise they may simply repel each other, or if they have the correct nature simply annihilate each other. Dislocation interactions form the basis for work hardening in materials, as interacting dislocations make it harder for slip to occur.

Occasionally dislocations can change planes, this is known as cross slip, when the dislocation changes the plane it is on at a single point, or dislocation climb.
when the dislocation line partly moves onto a new but parallel plane. The points at which the dislocation changes direction are known as jogs.

When two dislocations interact, part of one dislocation is slipped in another plane from the rest, and the two ends where the slip occurred become pinned, where a section of the dislocation is now perpendicular to the dislocation line. This can also occur due to thermal effects from the movement of atoms. These dislocation "jogs" can be a source of vacancies in the material, and the pinned section of dislocation can act as a Frank-Reed source (Frank 1980), creating additional dislocation loops on the new plane, increasing the dislocation density.

The dislocation density of a material describes, in units of dislocation length/unit volume, the amount of dislocations within a material; this will usually depend on how deformed a material is, and what processing has been done to it. As the dislocation density increases, dislocation interactions become more frequent, and these interactions further increase the dislocation density.

Due to the interactions between dislocations to reduce the total strain energy, during deformation they often form "cells" (Kuhlmann-Wilsdorf 1982), walls or lines of dislocations concentrated on where slip has occurred in the material; these can then become "sub grains" areas of material slightly misaligned compared to the surrounding matrix, but not yet completely separate grains.

Dislocations are always present within a material, even after long periods of annealing, but the dislocation density is massively increased by deformation, this can have important effects for particle evolution.

2.5.2 Dislocations and diffusion

Dislocations are important to this work because they can have several effects on particle controlling processes. Firstly, due to the core of the dislocations being
an area of distorted lattice, it is possible for diffusion to occur more rapidly in the core of the dislocation than in the surrounding matrix, this is known as “pipe diffusion” as the dislocation effectively acts a pipe for atoms (Picu & Zhang 2004). This process is most effective when dislocation networks have been built up by deformation of the material. (Love 1964).

Secondly the interactions between dislocations create jogs, which can then create vacancies (Seitz 1952). This has been studied in detail for steels, and the effect on the vacancy concentration from deformation can be relatively large. (Ungár et al. 2007).

Vacancies are empty spaces within the crystal lattice where there would normally be an atom. Like dislocations they are defects within the lattice which are always present to some extent, but the previously described interactions effect the concentration significantly. Vacancies greatly increase the both the self-diffusion rate within a material, and the diffusion rate of any substitutional solute atoms, such as Mn in aluminium. This is because without a vacancy, any atom must effectively “swap” places with another in order to move a single atomic spacing, if a vacancy is present it can instead simply fill the vacant space, leaving a vacancy behind for no net change in energy. This is very important for the diffusion of Mn in the alloys considered in this work, as the diffusion coefficient of manganese is very low.

The combined effect of pipe diffusion and vacancy concentration enhancement is to increase the diffusion rate within the material during deformation; this will accordingly increase the rate of any diffusion controlled processes, such as coarsening. This type of effect has been demonstrated in processes such as ultrasonic welding, where effective strain rates can be very high (100s⁻¹) (Gunduz et al. 2005) and has also been proposed as enhancing diffusion, and
hence coarsening, in lower strain rate tests (Rofman & Bate 2010) (Deschamps et al. 2012).

2.5.3 Deformation mechanisms and particles

As previously discussed dispersoid particles are nucleated on dislocations within the material, therefore deformation leads to an increase in the availability of nucleation sites in the material. Deformation can therefore be used to cause or enhance the precipitation of a fine dispersion of particles. This is used as part of the processing route for some alloys, where precipitation is very difficult, but has also been shown for Al-Mn alloys that had a super saturation of alloying elements still present (Chen et al. 2006),

Other work has shown that this can occur when the deformation and heat treatment occur sequentially or simultaneously, and the nucleation enhancement effect has been shown to be inversely proportional to strain rate (Embury et al. 2003). This suggests that it would be possibly for new particles to precipitate on these dislocations if a driving force is present, this could come from a reduction in temperature, as would occur during rolling. Additionally this work demonstrated that some particles can be dissolved by deformation mechanisms, rather than precipitated. This has also been found in highly deformed heat treatable alloys, where the expected fine precipitates are not found after equal angle channel die pressing (Gutierrez-Urrutia et al. 2005).

Due to the density of the dispersoids, particle-dislocation interactions occur relatively frequently. The particles will have an effect on the movement of the dislocations within the material, usually having the effect of pinning the dislocation in place, if the dislocation has a large enough force applied by the external stress it can pass around the particle, this can then create a dislocation loop around the particle, which can then create a Frank-Reed source, just like a jogged section of dislocation. In a distribution of particles the dislocation
pinning potential of a particle is inversely proportional to the mean size, as this determines the particle spacing (assuming a constant total volume of particles). The particle spacing controls the radius of curvature of dislocations, which must bend through the gaps. As the dislocation bends, its length increases and this costs energy. The smaller the gap between the particles, the greater the force required on the dislocation to bend around them. Additionally the curvature around the particles will be tighter with smaller particles, also resulting in a higher force required to move the dislocation.

The dislocations may also have an effect on the particles themselves. As the semi coherency of the particles is controlled by the fit of the interface, dislocations on this surface may lead to a breakdown of the coherency and an associated increase in the surface energy of the particles. A loss in coherency of a particle has been found to increase coarsening rates due to increase in surface energy (Iwamura & Miura 2004). It is logical to assume that other surface energy dependant processes such as spheroidization will also be enhanced. Coarsening enhancement has also been attributed to the enhanced diffusion due to increased vacancies (Deschamps et al. 2012) where the coarsening rate was found to increase linearly with strain, rather than strain rate.

Dislocations also interact with solute atoms within the matrix. As both the dislocation and the solute atom have an associated strain field surrounding them they can interact in different ways. Solute atoms can be attracted to areas in the dislocations strain field where they will act to reduce the overall strain, this in turn can act as a drag on the dislocation, as it can no longer move for no net change in energy, instead the dislocation must move, then “wait” for the diffusing solute atoms to “catch up”, this is referred to as dislocation damping, as the effect is similar to a mechanical damper on motion (Rickman 2002). Dislocations have also been suggested to cause segregation of solute within the matrix, due to this elastic interaction and the enhanced diffusion at the
dislocation core (Mortlock 1960). It is logical that this would also have the effect of increasing particle precipitation on dislocations, as an enhanced local concentration along with faster local diffusion conditions will allow rapid particle growth.

It has been proposed that the energy associated with the formation and existence of defects such as dislocations can be incorporated into the Gibbs free energy equations, and as such can be accounted for in a thermodynamic calculation of the system (Kirchheim 2007b). Thus the effects on solute segregation due to these defects can be calculated, and incorporated into models. (Kirchheim 2007b).
2.6 Mathematical modelling of microstructural development

The use of modelling within materials science is an increasing area of research. Modelling allows the simulation of processes and complex systems without having to perform experiments where experimental work would either be difficult or impossible due to the nature of the subject. Physically based models can calculate the effect of changing process parameters on the outcome, once the model has been calibrated to initial results. This can be especially important for industrial processes where “test” runs would be time consuming and expensive. In the scope of this project, the areas of modelling that are of interest are physical deformation, particle nucleation and growth, and microstructural development. One objective of the aluminium industry has been to create a “through process model”, one which can predict the properties of the final material from the properties of the feed material and knowledge of the process parameters. This has been done in previous work by linking the inputs and outputs of separate process models (Neumann et al. 2004).

The type of model created usually depends on the system being examined, Monte Carlo methods are one popular approach for simulating atomic scale interactions, for example the beginnings of nucleation or interactions around dislocations (Eivani et al. 2012). These models aim to simulate microstructural processes by simulating each atom, diffusivity is simulated by varying the probability of an atom to “jump” to an adjacent site. Monte Carlo models have been successfully used to simulate atomic or atomic cluster size processes, but would require vast computational power to model a statistically significant number of particles

Phase field models are used to examine the movement of interfaces within a system, for example solidification fronts, these are usually complicated and do not model large scale systems (Deschamps & Perez 2010). Therefore constitutive models tend to be used when examining a particle population.
2.6.1 Constitutive Microstructural modelling

The project aims to develop a constitutive model to predict the effect on hot rolling processing conditions on the development of dispersoid particles within 3XXX series alloys. To do this, existing work on modelling dispersoid development will be expanded upon, as modelling of dispersoid evolution during heat treatment has been performed for several types of alloy (Suni et al. 1996)(J. Robson 2004), and is usually considered to be accurate when correctly calibrated with experimental results. To date these models have so far ignored any deformation effects in their calculations.

The models used to simulate dispersoid population evolution are usually constitutive models. Constitutive computer models of material development work by combining equations which represent the various processes occurring within the material into one single program, which calculates the solution to the equations according to the inputs given. These inputs will be material constants, calibration constants and the process parameters such as time and temperature.

Constitutive models have been used to examine the phase transitions that occur during the heat treatment of alloys containing Al-Mn particles (Kuijpers et al. 2003) but in different alloy systems to those examined in this work.

Suni and Shey’s work on particle evolution in 3XXX series produced a model which gave a satisfactory fit in terms of predicted particle population for alloys within the upper range of Mn content for this work, this was shown by comparing the predicted conductivities to those measured in material (Suni et al. 1998). This type of model could be used to predict the general particle statistics after heat treatment, and could be modified to include deformation effects from a separate model.
2.6.2 KWN models

More recent work on modelling dispersoid evolution has used the mathematical approach first proposed by Kampmann and Wagner,(Kampmann 1991) This approach simplifies the particle evolution process somewhat in order to facilitate calculation.

- Time is calculated as a series of steps rather than as a continuum, this allows calculations to be made for each of these steps.
- The particles are divided into a set of size classes (“bins”) rather than a continuous distribution.
- For each time step the number of particles is calculated using nucleation theory for each timestep. Coarsening occurs naturally in the model as the mean solute level in the matrix falls, leading to dissolution of the smaller particles at the extreme of the larger areas.
- Growth is assumed to be diffusion controlled by a single species.
- The effect of particle curvature on the interfacial composition is accounted for (the Gibbs-Thompson effect).
- The change solute level within the matrix is calculated for each timestep using the mean field approximation.
- The model runs through the calculation for each timestep, then reverts to the start of the calculations and updates, until the end of the time calculated.

This model has been used for the simulation of the development of Al-Sc particles both during heat treatment (Robson & Prangnell 2003) and from there has been expanded upon to examine the overlap of particle evolution processes (Robson 2004), and the factors controlling the balance of these processes.
This work modelled the original KWN framework to adapt the timestep function. This work produced predictions of the number density and mean radius of the dispersoid particles concerned after homogenisations of different lengths at 500°C.

![Graphs showing KWN predictions and experimental results](image)

**Figure 14 KWN predictions and experimental results of number density and mean radius of dispersoids (Robson & Prangnell 2001)**

The predictions made fall within the experimental error of the observation, showing that the model is as accurate as it can be when experimental calibration is needed.

Work by this research group has applied this model to complex processing routes such as friction stir welding (Kamp et al. 2006) and to analysing the precipitation of dispersoids in Al-Mg alloys and the formation of PFZs in these materials (Cai et al. 2007). Kamp used the model to predict the precipitate
evolution in material surrounding a weld, and used differential scanning calorimetry to acquire best-fit values to calibrate the model.

Figure 15 Comparison of precipitate and PFZ size predictions and measurements for different cooling rates (Kamp 2006)

Again the modelling predictions (Figure 15) were very close to the experimental measurements, although not always within the experimental error. These examples show that the model itself can be made into a predictive tool, but that experimental calibration is required in order to make accurate predictions.
Other work using this form of model has investigated the precipitation of second phases in heat treatable 6XXX series alloys (Samaras 2006), and to make predictions of the physical properties influenced by these particles, notably precipitation hardening (Wu & Ferguson 2009).

Recently this framework has been by other researchers used to model the development of the particle populations covered here. This work used a KWN model linked to a CALPHAD (calculation phase diagram) database for thermodynamic data. This model was used to predict not only the dispersoid evolution, but also the evolution of the constituents and the composition of the inter dendritic spaces. This model showed good agreement with experimental data gathered by SEM and EPMA for A3003, successfully predicting the size range of the dispersoids and the shape of the distribution Figure 16.

![Figure 16 Measured and predicted particle distributions after a 1h 600°C hold in AA3003 (Du et al. 2013)](image_url)
While the work by Du (Du et al. 2013) effectively models the effect of changing the Mn and Si concentration for heat treatments with a ramp and hold, the two stage heat treatments used in industry and the work discussed here were not modelled, so the particle populations cannot be directly compared. However it does demonstrate the effectiveness of this model in simulating the system to be examined.

The KWN model has several advantages for this project, as it is a constitutive model based on the actual system; behaviours such as particle nucleation, growth and coarsening are included by default, emerging out of the physically based calculations. While this model has been very successful in simulating thermal treatment, modifications will be required to account for deformation effects. This will take the form of alterations to the nucleation site density calculations and to the calculation of diffusion rates. The model does however make some assumptions and simplifications, for example the model assumes particles are spherical, which the dispersoids discussed here are not.
2.6.3 Modelling Deformation Effects on diffusion

While considerable work has been previously conducted on modelling microstructural development during thermal treatment, the effects of thermo-mechanical treatments have not been closely assessed. To do so any model must simulate the evolution of the system over time due to temperature, while accounting for the extra changes due to deformation. The most important effect for the alloy systems considered in this work is the increase in diffusion rates during deformation. This has been previously studied for steels (Militzer et al. 1994).

The work by Militzer et al investigated the relationship between deformation mechanisms, the production of jogs, vacancy production and dislocation density, and the effect of these on microstructural development when material is deformed at higher strain rates (<0.1s\(^{-1}\)).

This work created a phenomenological model by deriving and linking the equations corresponding to the different processes taking place within the material. The original model is broken down and explained here, while the version created and modified for this work is explained in chapter 6.

Firstly a calculation for the vacancy production rate due to deformation is performed, this is used to determine the steady state concentration during deformation and the concentration after deformation, and the deformation parameters are also used to calculate the dislocation density. The production rate of excess vacancies is given by.

\[
\Pi = \left( \chi \left( \frac{\sigma \Omega}{Q_f} \right) \varepsilon^p \right) + \zeta \left( \frac{c \Omega}{4 \beta^3} \right) \varepsilon^p
\]
Where $\varepsilon$ is the strain rate, $\sigma$ the stress, $\chi$ is a mechanical constant, set as 0.1, $\Omega$ is the atomic volume, $b$ the Burgers vector, $Q_f$ the vacancy formation energy, and $\Pi$ is the vacancy production rate. The parameter $\zeta$ accounts for the neutralization effects produced by the presence of vacancy emitting and adsorbing jogs. This effect was expected to increase with jog concentration, so that the thermal contributions are effectively eliminated. This was simulated by setting:

$$
\zeta = 0.5 - C_j \text{ when } c_j < \frac{0.5}{\zeta_0}
$$

$$
\zeta = 0 \text{ when } c_j > \frac{0.5}{\zeta_0}
$$

The constant $\zeta_0$ was set to around 10, so that a jog spacing of around $20b$ would result in complete neutralization of the thermal contribution. The thermal jog concentration $c_j$ was calculated as:

$$
c_j = e^{-\frac{E_j}{kT}}
$$

Where $E_j$ is the jog formation energy, $k$ the Boltzmann constant and $T$ the temperature in Kelvin. The jog formation energy was estimated to be:

$$
E_j = \frac{\mu b^3}{4\pi(1 - v)}
$$

Where $\mu$ is the shear modulus and $v$ the material’s Poisson’s ratio. This allows the calculation of the excess vacancy production rate; however the change in
concentration is also controlled by annihilation. The annihilation of vacancies occurs at sinks such as grain boundaries and dislocations and is a diffusion controlled process. The rate \( \eta \) depends on the vacancy supersaturation \( c_{ex} \), the sink density and the vacancy diffusivity, such as

\[
\eta = \frac{D_v \rho}{\kappa^2} c_{ex} + \frac{D_v}{L^2} c_{ex}
\]

Where \( \rho \) is the dislocation density, \( L \) the grain size and \( \kappa \) a structural parameter describing the dislocation distribution, equal to 1 for a homogeneous distribution and around 10 for a cell like structure. The vacancy diffusivity, \( D_v \), is calculated using the typical Arrhenius equation:

\[
D_v = D_{v0} e^{\frac{Q_m}{kT}}
\]

Where \( Q_m \) is the vacancy migration energy, this then allows the production rate of excess vacancies to be calculated as:

\[
\frac{dc_{ex}}{dt} = \Pi - \eta
\]

Or alternatively as:

\[
\frac{dc_{ex}}{dt} = \left( \chi \left( \frac{\sigma \Omega}{Q_f} \right) \varepsilon^* + \zeta \left( \frac{c_j \Omega}{4b^2} \right) \varepsilon^* - \frac{D_v \rho}{\kappa^2} c_{ex} - \frac{D_v}{L^2} c_{ex} \right)
\]

Integrating to calculate the instantaneous concentration gives:
\[c_{ex}(t) = \left(\frac{\chi\sigma}{Q_f} + \frac{\zeta c_j}{4b^3}\right) \Omega(\varepsilon(t)) - D_v \int \varepsilon(\phi) \left(\frac{\rho(\phi)}{\kappa^2} + \frac{1}{L^2}\right)x e^{-D_v \int \frac{\rho(\phi)}{\kappa^2}} d\phi \]

\[-\frac{D_v(t - \phi)}{L^2}\] \[d\phi\]

With \(\phi\) and \(\varphi\) as integration variables. For the time dependence of \(\rho\) the relation used was:

\[\rho(t) = \rho_s - \left(\rho_s - \rho(0)\right)e^{-t/\beta}\]

Where \(\rho(0)\) is the static dislocation density and \(\rho_s\) the steady state dislocation density during deformation, which was estimated from the geometrically necessary dislocation density:

\[\rho_s = \left[\frac{\sigma}{b\mu}\right]^2\]

The characteristic time \(\beta\) is linked to the demotion conditions and the material parameter \(\beta_0\) by the equation:

\[\beta = \frac{\sigma}{\beta_0\varepsilon^o}\]

At a constant strain rate, the excess vacancy concentration will reach a steady state value \(c_s\). Setting the rate of change of the vacancy concentration in eq X to zero, and \(\rho\) to \(\rho_s\) gives:
\[ c_s = \left( \frac{X\sigma}{Q_f} + \frac{\zeta c_j}{4b^3} \right) \left( \frac{\rho_s}{\kappa^2} + \frac{1}{L^2} \right)^{-1} \frac{\Omega}{D_v} \varepsilon^* \]

This suggests that \( c_s \) increases linearly with strainrate. In reality the increase is smaller, as both \( \sigma \) and \( \rho_s \) are strainrate dependant. This was approximated using a creep power law:

\[ \varepsilon^* = A e^{\left( -\frac{Q_{def}}{kT} \right)} \sigma^n \]

Where \( A \) and \( n \) are empirical constants and \( Q_{def} \) is an experimental activation energy. In the case where vacancy annihilation occurs mostly at dislocations, such as a high strainrate deformed material, \( c_s \) can be calculated as:

\[ c_s = \frac{\kappa^2 \pi \Omega}{D_v} A^{1/n} e^{\left( -\frac{Q_{def}}{kT} \right)} X \left( \frac{X b^2}{Q_f} \varepsilon^* \left( 1 - \frac{1}{n} \right) + \frac{\zeta c_j}{4b} A^{1/n} e^{\left( -\frac{Q_{def}}{kT} \right)} \varepsilon^*(1-2/n) \right) \]

Militzer et al. used this equation to show how the steady state vacancy concentration was affected by deformation conditions, shown in Figure 18.
To calculate the enhancement of diffusion by vacancies, it is necessary to calculate the concentration of thermal vacancies $c_{th}$.

$$c_{th} = 2.7e^{-\frac{Q_f}{kT}}$$

The effective self diffusion $D^*$ can then be calculated as:

$$D^* = D_b \left(1 + \frac{c_{ex}}{c_{th}}\right)$$

Where $D_b$ is the bulk diffusion coefficient calculated from

$$D_b = D_0 e^{-\frac{Q}{kT}}$$
This gives the enhancement due to vacancies, however it is necessary to also consider the role played by pipe diffusion. Including the pipe diffusion contribution the total diffusivity, $D$ was calculated as:

$$D = D_b (1 + \frac{c_{ex}}{c_{th}} + \frac{g D_p}{D_b})$$

Where for a dislocation core containing 2 atoms:

$$g = \frac{2\Omega \rho}{b}$$

And:

$$\frac{D_p}{D_b} = e^{\frac{q - 0_{gb}}{kT}}$$

Militzer et al then used these equations to calculate the enhancement of self diffusion for steady state conditions ($C_{ex} = C_s, \rho = \rho_s$).
This shows that as strain rate increases above 1, the relative influence of vacancies begins to dominate the enhancement of diffusion, while at lower strain rates pipe diffusion plays the larger role (Figure 19).

Once the diffusion rate is known, a traditional time-temperature based model can be used to calculate the microstructural model is used.

This work focuses on steels and so the constants and some of the equations are not applicable to aluminium, however the basis of this model will be used for the creation of the deformation section of the model produced in this work.

The work by Militzer uses a method of calculating the stress within the material which will need to be altered upon by including work on aluminium deformation. There has been significant work on developing aluminium deformation models for processes such as mechanical welding. This provides a different equation for the stress and constants for various types of alloy are available within the literature (Tello et al. 2010) which should give a more accurate result than the method used by Militzer.
Other work on diffusion within the cores of dislocations may help with improving the model, atomistic studies on the mechanism of diffusion in dislocations provides information on how the temperature effects these processes (Purja Pun & Mishin 2009), and work on the diffusion of Mg atoms within aluminium suggests that pipe diffusion will make a significant contribution (Picu & Zhang 2004). The higher temperatures and lower diffusion rate of Mn compared to Mg for the alloys in the presented work mean that both vacancy assisted and pipe diffusion should take place to some extent. Other works have examined the annihilation of vacancies and the mechanism by which an excess vacancy concentration can be removed (Svoboda & Fischer 2011).

Once a model for the post heat treatment microstructure has been created using the aforementioned KWN framework, sections of these deformation models can be incorporated as modifications or new calculations in order to add a deformation influence to the thermal based KWN model.
Chapter 3-Experimental

This chapter details the techniques used in performing experiments in the course of this research, along with the methods used to extract and process data on the particles.

3.1 Material

All of the experiments covered in this thesis used material provided by Novelis intended specifically for the research group currently investigating different areas of the production process. This material was cast at Novelis Kingston in the form of small DC cast billets, three alloys were cast, all with the same level of Fe and Si additions but with varying levels of Manganese. The exact compositions, measured by taking an average of 5 optical emission spectroscopy measurements for each are given in Table 2. This method of production ensured that the material had a microstructure most similar to that in commercially produced material. Once cast the billets were scalped, that is the faces of the billets were machined away; This was done for two reasons, firstly it provided a flat and even surface to measure and cut samples from, secondly it removes the region of material that has undergone the fastest cooling rate and so has the highest level of macro segregation and residual stress.
Table 2 Composition of supplied materials (wt%)

<table>
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<tr>
<th>wt%</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Ni</th>
<th>Si</th>
<th>Zn</th>
<th>Al</th>
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<td>0.3562</td>
<td>0.0007</td>
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<td>0.0004</td>
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<td>0.0014</td>
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<td>0.0019</td>
<td>0.1571</td>
<td>0.0021</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Before the material was received some modelling of expected phases and compositions was done using Jmat Pro. This software can calculate the expected equilibrium composition of an alloy in terms of phases, and the composition of those phases, for a temperature range. It can also be used to calculate the expected as cast composition by using a Scheil-Gulliver solidification model (Saunders et al. 2003). This modelling was done for each of the three alloys, and the results were used to design a range of heat treatments for the alloys which are discussed in chapter 5. This modelling was also used to provide data for the kinetic model created as part of this work, which is discussed in chapter 7.

Due to the size of the billets, the first stage in preparing heat treatment samples was to cut 20 mm thick sections from each billet on a large chop saw to create more manageable pieces. Then 20x20x20mm pieces were cut for each alloy and heat treatment to remove any effect of sample size on the effectiveness of the heat treatment.

For isothermal heat treatments, the samples were placed into the centre of a recirculating air Carbolite furnace that had stabilized at the required temperature, and left until the desired time had elapsed. For samples that
required a ramped or variable temperature, the furnace was programmed to follow the exact heat treatment plan, before the samples were placed inside and the programme started and monitored. All samples were quenched in water immediately on removal from the furnace, in order to freeze the microstructure from the higher temperature.

3.2 Preparation

In order to examine the results of heat treatments, the samples were prepared for both optical and electron microscopy. The first stage of specimen preparation for both of these techniques is to cut a smaller section of the sample off, using either the chop saw or an Accutom machine. This is done in order to expose the section through the sample which is to be observed. This sample was then mounted using a resin, for the majority of the samples examined this was a cold setting epoxy or polyester resin, used to avoid any thermal effects that may occur if a thermosetting mount was used. An epoxy resin was also selected due to its inertness for the use with electrolytic etches.

![Figure 20 Epoxy resin sample mounting](image)

Once mounted, the samples were ground and polished on a Struers polishing machine. All samples were hand ground using a succession of silicon carbide papers from 180 grit through 320, 600, 800, 1200, 2400 and finally 4000 grade, with samples being cleaned between each stage to remove any loose particles that could cause scratches later. The rougher grades were also used to remove any sharp edges from samples. Once a well ground surface was achieved, the samples were polished using polishing cloths embedded with diamond paste. 6 and 3 micron diamond pastes were used, and samples cleaned with a detergent.
and warm water to remove the residue of lubricant and diamond paste from the sample. Once polished with diamond samples a final polishing step was performed using OPS, a colloidal silica solution. This was done for a longer period of time in order to give a very smooth surface for microscopy. Once sufficiently polished samples were then cleaned with detergent and warm water followed by a rinse with ethanol. It was found that an ethanol rinse in an ultrasonic bath was the most successful method of completely removing any OPS residue.

Polished the samples were then prepared in different ways for the specific type of microscopy. Samples for optical microscopy were etched, whereas samples for SEM were left unetched but were attached to aluminium stubs and a conductive path of silver paint applied, to prevent charging of the sample in the microscope.

Barkers etch was used to show the microstructure under optical microscopy, the etch consists of HBF in solution with water, and is used as an electrolytic etch, as a current is applied and a oxide layer grown, rather than material being removed. This etch reveals both the microstructure of second phase, and if cross polarised light is used it gives contrast between different grains, allowing the grain size to be measured. The parameters for etching with Barker’s reagent were an applied potential of 30V DC with the samples as the anode and around a 40 second application, dependent on the samples response.

### 3.2.2 Electro polishing

For the very high resolution imaging in the SEM using techniques such as the through lens detector (discussed in 3.3.3) it is advantageous to use electropolishing to improve the surface finish of the samples. This uses a chemical reaction to remove a layer of material from the surface. In particular
Electropolishing removes the deformed surface layer created during cutting and polishing.

For these aluminium alloys electropolishing was performed in a 30% nitric acid solution in methanol, cooled to -30°C. To prepare this, the necessary volume of methanol was placed in a beaker, inside a shallow dish on a stirring plate. The stirrer was used to agitate the fluid, while liquid nitrogen was added to the shallow dish to cool the solution. Once the temperature was below -30°C, the acid was added slowly while the solution was continually stirred. Liquid nitrogen was added whenever the temperature rose above -30°C to avoid a runaway reaction. The same method was used to prepare the electropolishing solution for TEM preparation.

![Electropolishing equipment](image)

Once all of the acid was added and the temperature stabilized, the samples could be electropolished. The sample was held in a pair of tweezers attached to a DC power supply and a voltage of 12V was applied to the sample with the other electrode in the solution itself. The samples was gently oscillated in order to remove bubbles from the surface, and immersed for 10 seconds, before being rinsed in two consecutive methanol baths to stop any reaction. The samples were then examined under an optical microscope to check the surface finish.
3.2.3 TEM sample preparation.

For TEM it is necessary to produce very thin samples which will allow electrons to pass through the sample. This is done by mechanically thinning a sample followed by a twin-jet electro polishing technique. First a thin (<1mm) slice of the sample was cut off using an Accutom cutting machine. This was then ground on 600 grit paper until its thickness was below 500µm, then 1200 grit until the thickness is around 200µm, before a quick final polish on 4000 grit to give a smooth surface. Once thinned, 3mm discs were pressed from the samples using a punch.

Once the foil discs were created they were further thinned using a Struers twin jet electropolisher. This uses jets of electrolyte to thin the sample further until a very small hole is created at the centre, the electrolyte used is prepared in the same manner as for SEM electropolishing, but is then put into a bath, on top of which sits the twin jet machine. The correct voltage for electropolishing is found by using a scan function, and the sample is then polished until the apparatus detects a hole. The samples were then examined using an optical microscope to assess the surface finish prior to observation in the TEM.

3.3 Microscopy

3.3.1 Optical microscopy

For optical microscopy a traditional reflective light microscope was employed, using 10x, 20x, and 50x objective lenses. Optical microscopy was mainly used for the examination of the as cast and heat treated microstructures, in order to examine the evolution of the constituent particles.

The use of cross polarised filters allows the examination of the grain structure, as the different orientations of grains grow different thicknesses of oxide layer, which in turn cause a difference in birefringence which leads to extinction for different wavelengths of light when view under cross polarised filters.
3.3.2 Scanning Electron Microscopy

Several SEMs were used in the course of the project; the majority of the work was conducted on a Philips XL30 and Sirion FEG-SEM, with some use of FEI Magellan XHR and Quanta microscopes later on when they became available. The particle data presented is all from Magellan Images; however the samples had first been analysed on the Sirion giving similar results. All SEMs operate on the same principle, but there are some fine details which will be expanded upon where relevant.

Field emission gun (FEG) SEMs use a sharply pointed electron emitter in close proximity to an electrode with a several kilovolt potential difference, so that field emission of electrons occurs to produce the electrons for the beam in the microscope, this creates a narrower beam with a higher current density than a standard thermionic emission electron source. This allows for higher resolution imaging within the microscope along with reduced noise. The electrons emitted by the gun are then accelerated and focused onto the sample by a series of magnetic fields.

On impacting with the surface the electrons loose energy through repeated collisions with the electron shell of atoms, penetrating into the material. These collisions produce “secondary” electrons via inelastic scattering. As these secondary electrons are low energy only those produced very close to the surface can escape the surface of the material. It is these escaping secondary electrons that are used to form a standard SEM image. On a polished sample this usually highlights any raised areas where there is harder material, for example second phase particles. This technique is useful for examining surface features but is less helpful for examining the fine dispersoids concentrated upon in this work, as there is often little contrast.

If the accelerating voltage is sufficient, some electrons can impact the nuclei of atoms and be “backscattered”, reflected almost straight back towards the
source. This happens more often with atoms with larger nuclei, and so the intensity of the backscattered electrons gives relative information about the elemental composition of what is being examined. There is however a downside to this technique as there is a significant “interaction volume” from which the backscattered electrons can come from, which must be considered when examining the images produced. This method of imaging also gives contrast from the orientation of the matrix, as fewer electrons will be backscattered if the beam is parallel to a close packed plane, due to fewer collisions.

On the Magellan SEM a “through lens detector” can also be utilised, which creates an image from the electrons that pass back through the lens. This can also detect backscattered electrons, and can be used with very low working distances and lower accelerating voltages, allowing for better resolution than standard backscattered electron images.

While high quality images are usually created by a single slow scan of the observed area, it is also possible to integrate a series of images on this microscope, this removes noise and improves the contrast observed in the images. As a faster scan speed is used, this reduces localised charging effects, as the beam spends less time on each point.

Magellan SEM conditions for images for particle analysis were an 8kV accelerating voltage and a 5mm working distance and a 1.6nA current. Each image viewed a field 12.7µm wide.

### 3.3.4 Transmission Electron Microscopy

The samples were then examined in the Tecnai TEM, utilising a 100kV accelerating voltage, to obtain high magnification images of the dispersoids. Bright field images were used for examination of the particles, this method was used to reveal the dislocation structures around particles in deformed material.
3.3.5 Image analysis

In order to examine the particle population statistics, it was necessary to quantify the observed particles. This was done using the image analysis software package Image-J. In order to analyse enough particles at least 10-15 images were taken per condition, with each image containing around 200 particles. The images were taken from randomly selected regions, usually in a grid of images. While any obvious flaws such as pits or surface contaminants were avoided, constituents and their associated PFZs were not in order to accurately represent the average number density of dispersoids.

Once the images were obtained there were several steps to obtaining the particle statistics. Firstly the correct scale had to be set within the software, this was done using the scalebar from the microscope image. To process an image, firstly it had to be converted from an 8 bit greyscale to a binary image, this had to be done for each image individually, as the threshold required to highlight only second phase varied on the background contrast from the matrix. An upper threshold value was used to avoid selecting features such as the scalebar. Once suitable threshold settings were selected the “analyze particles” function was used, this allows a size range to be selected. To remove any effect of noise, a minimum particle area of 0.001 \( \mu \text{m}^2 \) was chosen, this corresponds to a 5x5 pixel square, or a particle with an 18nm equivalent radius. While some particles may be below this size, they would be indistinguishable from noise, and pixilation effects will have an overly large effect. For an upper size limit an area of 0.25 \( \mu \text{m}^2 \) was chosen to exclude small constituents that had been broken up. This was important as smaller constituents tend to be very rounded and accidently including them in the dispersoid analysis would alter the shape measurements. The stages of this process are shown in Figure 22 to Figure 24.
Figure 22 Backscattered SEM image before processing

Figure 23 Thresholded SEM image

Figure 24 Outline of selected particles from thresholded image
Once measurements had been made for each image they were combined for each condition examined, to have a dataset for each condition. From this, the median values for each of the particle parameters were calculated. The effective radius for each particle, which is not given by the software, was calculated as:

\[
\text{Effective radius} = \sqrt{\frac{\text{Area}}{\pi}}
\]

The aspect ratio calculated by the software compares the longest measurement of the particle to a measurement perpendicular to it, a method that is valid for these shapes of particles. Additionally, the number density and observed area fraction of the particles was calculated by dividing the number of particles and the total particle area by the total area examined, this allows both a comparison of these values along with a normalization values for comparing data later.

Constituents smaller than 0.25µm² were removed from the datasets, this was done by plotting a scatter plot of effective radius against aspect ratio, such as Figure 25. This usually revealed around 5 particles per dataset which had low aspect ratios, and were clearly demarked from the general population in terms of size, these particles were then removed from the dataset. While some constituents even smaller than this may remain, any constituent in the size order of the dispersoids will act and respond similarly to a normal dispersoid in terms of microstructural properties, so the distinction is largely irrelevant.
Figure 25 Scatter plot of aspect ratio vs particle radius of heat treated material (2 step +0.5h 450°C)

3.3.6 Stereology and volume analysis

In standard stereoscopy there exist techniques to convert a dataset created from 2 dimensional images into statistics for a three dimensional population of particles. These techniques account for the likelihood of sectioning through a particle. However these methods assume that the images taken are completely 2D slices through the particles, and that either the size or shape of the particles remains the same. As the images taken here actually each represent a thin 3D volume due to the interaction volume effect, these techniques are not appropriate. Additionally a large range of particle sizes are possible which may make this form of correction difficult.

Instead the assumption has been made that dispersoid imaged via SEM in this way appear as a projection of the outline of the particle, therefore representing the actual size in two dimensions. While this avoids the need for correcting any sectioning effects, it does leave the possibility that alignment of the non-
spherical particles changing the measured size, which is considered in chapter 6.

For this reason the number density statistics have also been left in terms of observed particles per µm² although this actually represents a number of particles in a volume 1 µm square with the depth of the interaction volume. Since the purpose of this work was to make a comparison between conditions viewed under identical conditions, rather than an accurate absolute prediction of number density, this approach is adequate here.

The size of the interaction volume can be estimated using Casino Monte Carlo simulation software, which calculates the probability of the electron interactions within the material, and thus calculates the probable depth of travel into the material. The software also calculates the probability of interactions with nuclei occurring, and therefore the number of electrons backscattered. It then produces a map of the simulated electron paths (Figure 26).

Figure 26 Interaction of incident electrons (Captured electrons in blue, backscattered electrons in red)
The simulations predict that for the conditions used in the Magellan SEM (8kV accelerating voltage, 1kV stage bias) Electrons will penetrate up to 500nm into the material, however backscattered electrons emanated from within 200nm of the surface, it can therefore be assumed that any particles observed are within this 200nm layer. As dispersoid particles are smaller than 200nm, the assumption that imaged dispersoids are seen as a projection seems reasonable.

This has also been used to estimate the volumetric density of particles, by assuming the particles measured represent the dispersion throughout this depth.
3.4 Thermomechanical simulation

In order to examine the role of deformation mechanisms on the development of particles, it was necessary to find a testing method that accurately simulated the conditions found during rolling. Several methods were considered. Actual hot rolling could be used, however the exact rolling parameters, especially the temperature, are very difficult to measure and control and the rolling equipment available cannot reach the high strain rates achieved during commercial hot rolling. Another method considered was plane strain compression testing. While this method has finer control of temperature and deformation rates, the process cannot be extended or repeated to simulated deformation over a longer time period, in order to examine the effect of time dependent processes, such as enhanced diffusion, on the particle development. The best choice for deformation testing was to use torsion testing to deform the samples, using the arbitrary strain path (ASP) machine at Sheffield. To support this work, some preliminary rolling tests were also performed.

As the strain rate of the rolling process is controlled by the rolling speed two samples were rolled at different speeds. Each received 5 10% reduction passes, one rolled at 0.152ms\(^{-1}\) and one at 0.076ms\(^{-1}\). As the temperature needed to be as close as possible to the heat treatment end temperature, the material was heated in a furnace back to the end of heat treatment temperature (500°C) before the first rolling pass, then stabilized again in the furnace, before the next pass. After the completion of the rolling passes, the material was quenched to preserve the microstructure.
3.4.2 ASP Torsion Testing

Torsion testing has been previously used to create large deformations in metals analogous to rolling (Wong et al. 1995; Wu et al. 1998). The Sheffield University machine was specifically developed to examine the effects of strain path on materials during processing (Angella et al. 2005), and has been previously used to thermomechanically test wrought aluminium alloys (Wynne et al. 2007; Lopez-Pedrosa et al. 2006)

The first stage of torsion testing was to prepare the required samples. These were cut from the provided billet according to plans provided by Sheffield University. The sample diagram is shown in Figure 27. The samples are similar to traditional cylindrical tensile specimens with a thin central section where the deformation occurs and thicker ends with flat sides where the sample is held. A hole for a thermocouple is drilled into the sample at an angle at the shoulder so that its tip is on the central axis just below the deformation zone. Once cut the samples were heat treated in the same manner with a programmed heat treatment followed by a quench as described previously.

![Figure 27 Torsion Sample Diagram](image)

The ASP machine appears similar to a large standard tensile testing rig. There is a fixed base which holds one grip, and an upper crosshead which has another grip. The machine has the necessary sensors and controls to perform normal
tensile or compression tests. The difference however is that the upper crosshead can also rotate around its central axis. This allows the torsional deformation of the sample. Additionally there is an induction coil and associated control system linked to thermocouples, which can be used to perform elevated temperature tests. There is also a controlled cooling system that can rapidly quench the sample at the end of deformation using water jets.

Setting up a torsion test is a lengthy process. Firstly if elevated temperatures are required the heating system must be calibrated so that the temperature at the centre of the sample is at the correct value. This is done by first heating a sample with an extra thermocouple at the centre of the deformed area. The heater is controlled by the shoulder thermocouple, placed in the hole marked r1 in Figure 27, and the target temperature is adjusted until the centre thermocouple is at the desired temperature for testing. This target temperature is then used for all further tests at this temperature, which are run without the additional thermocouple at the centre. Two temperature calibration tests were performed for this work, once for 500°C and once for 450°C in order to calibrate for both testing temperature used, the temperature needed for 500°C was 463°C, for 450°C the temperature at the shoulder thermocouple was 432°C.

Once the temperature had been calibrated, actual torsion tests were performed. The first stage is to place the sample in the correct orientation in the upper grip. This then had to be centralised using a set of Vernier callipers to measure the distance from each side to the sample. Then the sample was aligned with the axis of rotation, this is vital in order to remove any bending forces that could occur. This was done by rotating the crosshead repeatedly through 180°, while a fine measuring gauge measured the distance between the sample and the stanchion. By careful movement and controlled adjustment of the upper grip bolts, this was continued until the variation in this distance was reduced to less than 100µm and the sample was properly held in the grips.
The sample was then lowered through the induction coil, and a thermocouple placed in the drilled hole, before being attached with steel wire. The crosshead was then lowered further until the sample could be fastened in the lower clamp. The final stage of preparing the equipment was to re-centre the induction coil, align the cooling water jets and put the front cover in place.

Due to the novel nature of the testing, a new control programme for the torsion tests had to be created using the building blocks provided by the control software. The first stage was to remove any residual tensile load, and to zero the torsional displacement and load. The deformation test procedure consisted of a rapid heating stage (requested 100°C s⁻¹). During this stage, to remove the possibility of deformation and misalignment due to thermal expansion, the crosshead remained in vertical load control. Once the measured temperature had stabilised, the deformation program was begun. During this, the vertical displacement was locked. The deformation programs consisted of a clockwise rotation of an angle, followed by an anti clockwise rotation of the same angle; this was created as a loop that repeated multiple times, the rate of deformation was set in terms of °s⁻¹. The parameters used for this had to be derived from the outcomes and results of the first set of experiments, as it was found that sample failure was somewhat unpredictable, having no obvious relationship to deformation angle, speed or number. This is discussed further in chapter 6. Once the sample had reached the end of the cycle the system automatically quenched the sample, retaining the post deformation microstructure. Throughout the deformation process, the system logged the torsional and axial force and displacement, along with the temperature at 1024hz. Once quenched, the sample was removed from the machine and taken back to Manchester for analysis.
3.4.3 Torsion sample analysis

It is an unavoidable consequence of the type of deformation that the strain and strain rate experienced is inhomogeneous through the torsion sample. However, as discussed later, this can be used advantageously to provide a continuous variation in deformation across a single specimen. For the cylindrical samples tested here, the calculation for strain and strain rate is complicated and requires prior knowledge of material constants, however at a particular point, known as the “effective radius” it has been shown that strain and strain rate are independent of material constants and can be simply derived (Barraclough et al. 1973) This point is at 72.4% of the specimen radius out from the axis, and the strain is therefore given as:

\[ \varepsilon = \frac{0.724R\theta}{\sqrt{3\ell}} \]

![Figure 28](image_url)

Figure 28 Effective radius sectioning (introduction to asp) a, the location of the “effective radius” with the produced tangent plane in grey. b, the predicted strain gradient across the tangent plane (useable area between the dashed lines) (Introduction to ASP 2011)
Work conducted in the preparation of the machine calculated that a section taken through the sample at this point would have a 1mm wide area either side of the centre line with very similar deformation history, shown in Figure 28, which could be examined in a microscope to investigate the microstructure.

![Figure 29 FEA analysis of strain distribution through sample geometry performed by Sheffield University showing distributions a, at the surface b, through an axial section, c, through the tangential “effective radius” plane and d, a longitudinal section through the axis. (Introduction to ASP 2011)](image)

In order to examine the particle development it was decided to section the samples in two ways. Firstly the method of taking a section through the sample at 0.724 of the radius was used (Figure 29c), by mounting one half of the cylindrical portion of the sample in resin, then grinding and polishing from the
edge down to the “effective radius”. This creates the specimen seen in the bottom right of Figure 30. This will be referred to as a “longitudinal section”. Analysis of these specimens always looked at the area within 0.5mm of the centreline. These specimens provided data of material with a known strain and strain rate, using the basis of the calculations previously performed during the development of the machine, and has also been included in comparisons made across single samples as the 3.65mm point.

Secondly the samples also had a circular slice taken from the centre of the gauge, in order to examine particle changes along the radius, giving very similar thermal history but significantly varied mechanical history. This will be referred to as the transverse section. These samples were imaged in multiple positions at the centre, at the mid point (2.5mm) and at the edge (4.5mm). While the exact strain and strain rate cannot be derived for these positions, a qualitative comparison can be made across the sample, and comparison can be made between the same positions on each sample.
Figure 30 Torsion sample sections (polished areas in light blue) Transverse section top right, longitudinal section lower right
Chapter 4-Results

This chapter details the experimental results obtained during the course of this research, these consist of the pre and post heat treatment microstructures, the results of rolling experiments, and the results of torsion experiments, including microstructures, particle statistics and mechanical data.

4.1 Heat treatments

The first stage of the project was to find a primary heat treatment that produced a population of dispersoids within the material. These experiments also provided an understanding of the development of the microstructure.

The as cast microstructure in each alloy was imaged using optical and electron microscopy in order to allow comparison to be drawn against heat treated and deformed materials

PGL (0.1wt%Mn)

Figure 31 PGL (0.1%Mn) material as cast
The microstructure of cast PGL (0.1wt% Mn) seen in Figure 31 has a typical dendritic structure, with a small amount of second phase seen as the dark lines in the micrograph. The predicted equilibrium graph (Figure 32) shows that the possible phase relationship is very complicated, with a large number of different phases stable depending on the temperature range. The usual manganese containing dispersoid phase, \( \alpha \)-Al-(Fe,Mn)-Si, is only present at lower temperatures, while the constituent Al\(_3\)Fe phase is present at higher temperatures. This means precipitation of the desired dispersoid phase is unlikely in this alloy, although precipitation of the \( \alpha \)-Al-Fe-Si and \( \beta \)-Al-Fe-Si may be possible.

![Figure 32 Predicted equilibrium phase plot for PGL (0.1wt%Mn) alloy](image-url)
The PGM alloy has a larger amount of second phase, seen in Figure 33, with a similar microstructure to the lower manganese alloy. The predicted equilibrium phase relationship Figure 34 is considerably simpler, with only two equilibrium phases predicted over the temperature range. The α-Al-(Fe,Mn)-Si phase is present at higher temperatures, suggesting dispersoid precipitation during heat treatment should be possible.
The PGN microstructure has a further increase in the amount of second phase, with a smaller secondary dendrite arm spacing shown in Figure 35. The predicted phase equilibrium fractions (Figure 36) suggests that the Al₆Mn phase that makes up the constituent network is relatively stable, and that a large amount of α-phase may also be created, either by transformation or dispersoid precipitation.
The images show the microstructure for all three alloys is similar, with the main difference being an increase in the amount of second phase observed in the higher manganese alloys. The grain size is large in all cases, as would be expected since no grain refiner was used.

### 4.1.1 Isothermal heat treatments

The first heat treatments performed were isothermal heat treatments at 350°C, 500°C and 560°C, samples were removed from the furnace after 2, 4, 8, 24 and 48 hours. Below are micrographs and SEM images of samples of the PGN alloy after 48 hours at the specified temperature.
Figure 37 Optical (a) and backscatter SEM (b) image after 48h at 350°C for alloy PGN (1wt%Mn)
Figure 38 Optical (a) and backscattered SEM (b) images after 48h at 500°C PGN alloy (1wt% Mn)
There is little visible change in the population of constituents at any of the temperatures up to 560°C. Some particle break up has occurred and smaller particles have spheroidized, dispersoids are not visible in material treated at 350°C however there are very large dispersoids present in material treated at 500°C, there may also be some very fine dispersoids in the material treated at 560°C. This is likely because the equilibrium volume fraction of the dispersoid forming phase is higher at 500°C, and a long hold at 560°C will have allowed significant loss of dispersoids in favour of coarsening constituents.
In order to break up and reduce the volume fraction of constituents ramped heat treatments were tried, these used a 50°C/h ramp up to a temperature, followed by a 2 hour hold.

Ramping to 560°C as seen in Figure 40 had a more significant effect on constituents than a simple hold, however no dispersoids were visible. A ramp to 600°C also reduced the volume of constituents, and spheroidised the smaller particles. This is likely due to both diffusion of silicon into the particles causing transformation and break up, with some coarsening occurring. No dispersoids
were observed, this is consistent with the expected higher solubility of manganese at this temperature.

Figure 41 Backscattered SEM of PGN (1wt%Mn alloy after ramp and 2h hold at 600°C)
4.2 Two stage heat treatments

As isothermal and ramped heat treatments had not produced an even population of dispersoids two stage heat treatments were tried that first used a slow ramp of 45°C/h up to 550°C allowing for diffusion and break up of constituents, before then rapidly dropping to 450°C and holding for 2 hours to promote the nucleation and growth of dispersoids. Such a two step treatment practice is used in industry to enable both dissolution of constituents and precipitation of dispersoids. (Figure 36) shows that this will lead to a significant increase in the equilibrium volume fraction of $\alpha$-Al(Fe,Mn)-Si (the dispersoid phase), and a rapid change should promote nucleation rather than growth of pre-existing particles, as there will be a large driving force for nucleation on dispersoids.

Figure 42 (a&b) Backscattered SEM images of PGM (0.35wt%) after two step heat treatment

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As shown in (Figure 42) this two stage treatment proved effective in producing dispersoids in the PGM alloy, although the dispersoids were small and rather sparse. The dappled appearance of these micrographs is likely due to oxidation of the surface after polishing before microscopy was conducted.

![Figure 43(a&b) Backscattered SEM images of two step (550/450°C) heat treated PGN (1wt% Mn alloy)](image)

In the PGN alloy however the higher manganese content allowed for a much higher density of dispersoids to form (Figure 43), these are much closer to those found in commercial material, and are considerably smaller and more even in size than those produced by long isothermal heat treatment. A heat treatment
was trialled with higher temperatures for both stages. The purpose of this was to further increase the dispersoid volume fraction without an excessively long heat treatment. This 600/500°C treatment was performed and samples taken at intervals for conductivity measurements and micro structural analysis. These were compared to the results from the 550/450°C treatment already discussed.

Figure 44 Conductivity vs. time 550/450°C Heat treatment-PGN alloy (1wt%Mn)
The conductivity experiments (Figure 44) show that there is no change in conductivity below 350°C and only a slight increase at the maximum temperature. This suggests that the manganese in solid solution is remaining there during the ramp period. After the temperature drop conductivity is significantly increased; this corresponds to the nucleation and growth of dispersoids, removing elements from solid solution. It can be seen that the conductivity of the 450/550°C samples is higher after the drop than 500/600°C, indicating a higher volume fraction of dispersoids in the first case; however the level increases up to the 4 hour hold, indicating precipitation is ongoing. For the 600/500°C the conductivity rapidly stabilised after two hours, indicating a population of dispersoids that has reached an equilibrium fraction, but the dispersoids remain fine and well dispersed. This population of dispersoids should then only develop via coarsening if the temperature is held for longer at 500°C. Therefore the 600/500°C heat treatment, with a two hour hold, was used to generate a suitable dispersoid distribution for all deformation experiments. This will be referred to as the “two step heat treatment” from now on. All
subsequent work was performed on the PGN alloy (1wt% Mn) and all following figures correspond to this alloy.

![Backscattered SEM images of 600/500°C, 2 hour hold, 2 step heat treated PGN material (1wt% Mn)](image)

Examined closely, the microstructure formed by this heat treatment consists of a population of broken and spheroidised constituents, with a densely distributed population of dispersoids in the interdendritic spaces. Around constituents and grain boundaries there are precipitate free zones (PFZs) where the alloying elements have been absorbed by the constituents or have diffused.
along the grain boundaries. Within the grains are finely distributed dispersoids.

![Image of PFZs around constituents](a)

![High magnification back scattered SEM image of dispersoids](b)

Figure 47 (a) PFZs around constituents (b) High magnification back scattered SEM image of dispersoids

The dispersoids themselves are relatively fine and are rectangular in shape. There can be some variation in size across the interdendritic space, with those in the centre being relatively large, while those on the edge of PFZs are smaller,
this may be due to partial dissolution as a result of preferential coarsening of the adjacent constituents.

TEM images, shown in Figure 48 and Figure 49 show the dispersoids in the heat treated material to have sharp corners and flat sides, as would be expected for particles with a semi coherent interface.

Figure 48 Brightfield TEM image of dispersoids in 2 step heat treated material

Figure 49 Higher magnification brightfield TEM image of single dispersoid in 2 step heat treated material
Particle statistics after the two step heat treatment give a mean particle effective radius of 53nm, and a mean aspect ratio of 1.94 suggesting the particle in Figure 49 is representative of the population as a whole. The observed area fraction of dispersoids is 1.2% and the observed density is 0.85 particles per µm².

The dispersoid particle radii curve is positively skewed rather than forming a negatively skewed log-normal distribution, as would be expected of a population undergoing coarsening according to LSW theory where many smaller particles are being lost at the expense of larger dispersoids and constituents.

The aspect ratios of the dispersoids again show a positively skewed distribution, with the modal aspect ratio being around 1.5, but significant numbers of dispersoids having up to a aspect ratio of 3.
Figure 51 Dispersoid aspect ratios in heat treated material

This data was also used to conduct error analysis. As described in the experimental section the lower cut-off when measuring particles was 0.001µm², this equates to approximately a 10x10 grid of pixels. It is reasonable to assume that most of the error in measurement of particles would come from errors in judging the edges during thresholding. A 1 pixel over or under measurement would give a 10% error in particle size for the smallest particles examined.

Statistical errors also come into play during measurements of populations, the error in distributions can be approximated using methods such as the standard deviation for normal distributions, however the particle populations studies here are not normal, and were expected to shift and possibly significantly alter after deformation. Journal articles that have evaluated particle statistics in this system have not evaluated the errors in particle measurements (Du et al. 2013) (Li et al. 2012)(Y. J. Li & Arnberg 2003). This means a standard method of assessing the errors in the population is not available. Therefore a demonstration of the error by randomly splitting the data from one set has been used.
Data from the heat treated material was split into two equally sized sets by position on the micrograph the measurement was taken from (left and right) producing a random split. These datasets were then plotted as a set of histograms shown in Figure 52 and Figure 53.

These histograms show that the errors between sets is less than 10% for most of the range of particle sizes, with larger than 10% differences only occurring for sizes where the number of particles is less than 20. It should also be noted that the error will be increased in these figures as the dataset size is reduced. It is therefore reasonable to propose that a 10% error is applicable for particle sizes in the range of 0-0.1µm, or of an aspect ratio of below 3, above these sizes it is difficult to draw conclusions as the number of particles is too small.
Figure 53 Heat treated radius data split population comparison
4.3 Rolling

The next stage in examining the evolution of dispersoids was a set of rolling experiments. In order to compare different strain rates it is important to understand what controls the strain rate of deformation during rolling. The reduction percentage actual has little effect on the deformation rate if the same rolls are used, whereas altering the rolling speed has a significant effect. Below is a plot of the strainrate for reducing a sample in the rolling mill used by 10% reduction at possible rolling speeds attainable using the University of Manchester rolling mill. This was calculated using the simplified approach set out by Popoff (Popoff 1976) which averages the strain rate over the time a single position on the billet receives deformation.

![Graph showing strain rate predictions for University of Manchester rolling mill (10% reduction of 50mm thick plate)](image)

**Figure 54** Rolling speed strain rate predictions for University of Manchester rolling mill (10% reduction of 50mm thick plate)

As rolling a sample by a small reduction is simpler and less likely to result in uneven deformation during rolling, a reduction of 10% per pass was chosen, with two samples being rolled at 0.075ms\(^{-1}\) and 0.15ms\(^{-1}\), each for 5 passes.

The resulting microstructures show flattened, elongated grains within the samples, with micrographs taken of the rolling direction/transverse direction.
plane showing very large grains, while those taken of the transverse/rolling
direction plane showing diamond shaped, flattened grains. There is little visible
difference of the rolling speeds on the observed overall microstructure.

Figure 55 Optical micrograph of 0.075ms$^{-1}$ 500°C rolled material in (a)
Normal direction (b) Rolling direction
Figure 56 Optical micrograph of 0.15ms⁻¹ 500°C rolled material in (a) normal direction (b) rolling direction
Electron micrographs show the constituents have not been broken further by the deformation and have simply moved as the grains around them have deformed. The dendritic structure is still visible, although distorted.
The dispersoid population, seen in Figure 58, is also visibly similar to the post heat treatments population; PFZs are still present around the constituents. No change in dispersoid shape or distribution was qualitatively detected as a function of rolling speed (strain rate). The high magnification image (Figure 59) shows that the dispersoids have retained their elongated shape, and there is no indication of nucleation of new particles.
4.4 Torsion Testing

4.4.1 Initial torsion tests

These initial tests were used to gauge the capabilities of the ASP machine and to develop and refine the post deformation analysis techniques used, as all but one of the samples failed due to cracks, and multiple variables were changed for each test the results were mainly used to inform the next set of experiments, rather than to develop a quantitative analysis of deformation effects.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deformation rate (°s⁻¹)</th>
<th>Deformation angle (°)</th>
<th>Number of Cycles</th>
<th>Failed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>300</td>
<td>360</td>
<td>57</td>
<td>yes</td>
</tr>
<tr>
<td>1B</td>
<td>1500</td>
<td>180</td>
<td>100</td>
<td>no</td>
</tr>
<tr>
<td>1C</td>
<td>1500</td>
<td>180</td>
<td>~500</td>
<td>yes</td>
</tr>
<tr>
<td>1D</td>
<td>2000</td>
<td>90</td>
<td>~1000</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 3 Results of initial torsion tests

Figure 60 Optical Micrograph of edge and centre of deformed material transverse section (sample 1A)
The difference in microstructure between centre and edge material in the torsion samples is clear. In the centre of the torsion sample the large scale microstructure is still very similar to the post heat treatment microstructure, with large grains. At the edge of the sample the grains have been broken up and the previous dendritic microstructure has been destroyed. In particular the grain structure has been radically altered, and dynamic recrystallization has occurred.

Examining the longitudinal sample under SEM reveals a microstructure consisting of much smaller grains, usually in the order of 10µm in size (Figure 61). The constituents are broken up and distributed throughout the microstructure, often located along the new, dynamically recrystallized, grain boundaries.
The dispersoids in this material do appear to have been altered by the deformation. They are no longer seen to be plate like and instead appear rounded and more equiaxed. Additionally the width and continuity of the PFZ has been reduced with some dispersoids seen close to smaller constituents (highlighted).
Sample 1B $500^\circ s^{-1} 180^\circ$ Rotation, 100 cycles

![Image of Sample 1B grains]

Figure 63 Grains in torsion tested material Sample 1B

Sample 1B was the only sample in the first round of tests that did not fail, the backscattered electron micrograph shows that the grain size has again been significantly reduced, with the constituents broken and scattered. A pre-existing grain boundary with a PFZ is highlighted in red, while new grain boundaries pinned by dispersoids are also visible. This suggests new grains have formed nucleating on constituents as would be expected.

Sample 1C $1500^\circ s^{-1} 180^\circ$ Rotation, 500 cycles

![Image of Sample 1C SEM image]

Figure 64 SEM image of torsion sample edge (Sample 1C longitudinal section)
Figure 64 shows the beginning of failure cracks in this a sample, tested at 500°C 1500°s⁻¹, 180° 500 cycles. It can be seen that in the region of material near the sample surface, porosity and cracking has begun to occur. Once these cracks have begun to grow towards the axis of the sample, the deformation only occurs in the area between the crack and the axis, and the crack tip concentrates stress, further promoting crack growth and leading to failure of the sample. This sample failed after around 500 180° cycles.

Figure 65 a and b, Backscattered SEM image of grains in torsion tested sample (Sample 1C longitudinal section)
Looking closer at the microstructure in Figure 65, as with the previous samples the constituents have been broken up, with small grains being formed during the deformation, the dispersoids are again seen to be rounded rather than their original plate like shape. There is evidence of grain boundary pinning by dispersoids in the right of the micrograph (highlighted in yellow and expanded). PFZs appear around the clusters of constituents, but dispersoids are again seen close to lone particles.
After deformation at 2000°s⁻¹ by 90° rotation and 1000 cycles the microstructure again consists of broken up, clustered constituents, and small grains formed during the deformation. The grain size and morphology is not appreciably different to the lower strain rate tests. The dispersoids again appear rounded and there are some areas where an increased number density is apparent.

This sample survived for around 1000 90° rotation cycles before failure suggesting that cumulative strain may be the limiting factor for failure, as this sample had close to the same total strain as sample 1C.
4.4.2 Torsion 2

This set of torsion tests was intended to produce a set of deformed specimens deformed at different strain rates but having undergone the same cumulative strain and thermal history.

The first sample was a repeat of Sample 1D from the first round, this failed after ~800 cycles, whereas deforming by 360° resulted in very rapid failure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deformation rate (°s⁻¹)</th>
<th>Deformation angle (°)</th>
<th>Number of Cycles</th>
<th>Failed</th>
</tr>
</thead>
<tbody>
<tr>
<td>2i</td>
<td>2000</td>
<td>90</td>
<td>~800</td>
<td>Yes</td>
</tr>
<tr>
<td>2ii</td>
<td>2000</td>
<td>360</td>
<td>36</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 4 Summary of Torsion 2 failed tests

Samples i and ii failed so have not been analysed, since the level of strain experienced prior to failure, and the internal strain distribution will be varied due to cracking. These samples failures suggest that samples will fail rapidly if deformed by 360°, perhaps due to the level of tensile stress created, and that below this rotational angle cumulative strain is the controlling influence. Therefore all further tests we conducted with 100 180° cycles, as this gave the best balance between cumulative strain, minimising time spent while the machine switched direction, and avoiding failures.
Comparing the torque required to deform the material shows that while more force is required to deform the material at the higher strain rates, the difference is not very large. It can be seen that the torque amplitude reduces during
testing; this occurs in two stages, firstly there is a rapid drop off, then a slow decay. The rapid drop off is likely due to a slight softening effect, whereas the slow decay is likely due to the build up of defects within the samples, such as horizontal cracks.

![Figure 68 Temperature and Position vs Time (Sample 2A)](image)

The temperature during deformation is relatively stable, varying by no more than 1.5°C at the thermocouple throughout the deformation stage of testing.

![Figure 69 Torque vs time and position vs time 100°s⁻¹(Sample 2A)](image)
Close examination of the torque plot for the 100°s⁻¹ deformation, Figure 69 shows that the torque is constant during each deformation step. There is some relaxation at the end of each deformation step before the deformation is reversed.

![Cooling Curve 500°C](image)

**Figure 70 Time vs temperature during quenching (Sample 2A)**

The cooling curve shown in Figure 70 shows that the sample is rapidly quenched from the deformation temperature in around 1 second, it then holds at around 100°C for around 10 seconds before cooling further, this is likely due to the water spray boiling on the surface of the metal stopping any further heat transfer. This is important as it shows that any microstructural changes that have occurred will be preserved by the rapid cooling. By the time the specimen has cooled to 100°C, further microstructural change will be very slow.
Sample 2A 100°s⁻¹ 180° rotation, 100 cycles

The lowest strain rate sample in this set of experiments shows the dendritic arrangement of constituents has not been removed in the deformed material, however dispersoids appear rounded and slightly more densely packed than in the heat treated material,

![Backscattered images of longitudinal section 2A](image)

Figure 71 Backscattered images of longitudinal section 2A (a) low magnification (b) High magnification
The centre to edge comparison (Figure 72) shows that dispersoids at the centre remain unaffected, as would be expected for an area that receives no deformation. While edge dispersoids are somewhat rounded, there is no obvious difference in size.

Figure 72 Backscattered images of transverse section 2A (a) Centre (b) Edge
These qualitative comparisons can be backed up by quantitative analysis using the results of image analysis. Shown here for each sample are the particle size distributions in terms of particles per µm² and particle aspect ratios in terms of % of the total population.

![Graph showing particle density and effective radius](image)

**Figure 73** Particle size distributions for sample 2A

For this sample there is a decrease in the density of smaller particles in the more deformed material, seen in Figure 73, along with an increase in the density of particles larger than 90nm, the effect is relatively similar between the edge and the midpoint material. There is no clear explanation for the dip in density of particles around 50nm.

There is also a significant shift in the distribution of particle aspect ratios, with a stronger effect at the edge point than the mid radius. This correlated with the observations of rounded dispersoids in deformed material. It is notable that the strongest affect is seen in the longitudinally sectioned effective radius material.
Figure 74 Particle aspect ratio distributions for sample 2A
Sample 2B 500°s⁻¹

The results in terms of microstructure are very similar to sample 2A, in the transverse images, Figure 75, constituents are scattered, with dispersoids appearing rounded and slightly denser in population.

![Backscattered images of longitudinal section 2B](image)

(a) Low magnification  
(b) High magnification

Figure 75 Backscattered images of longitudinal section 2B (a) low magnification (b) high magnification

The centre and edge comparison, Figure 76, again show a change from flat, straight edge particles to rounded, oval particles, along with indications new population of very fine, round dispersoids.
Figure 76 Backscattered images of transverse section 2A (a) Centre (b) Edge
This data is somewhat harder to interpret, the centre data has an unusual dip around 50nm, similar to that seen in the mid and edge material of sample 2A. It is therefore difficult to draw comparison. It is possible that these results are due to an unusual area of material being tested, or due to differences between the surfaces of the material between microscope sessions.

The aspect ratios (Figure 78) fit with the observations from other samples; again there is a large shift towards rounder particles in deformed material. With an especially large shift in the particles observes in the effective radius sample.
Sample 2C 1000°s⁻¹

Scattered constituents are visible in the transverse images, Figure 79, while dispersoids are again seen to be rounded, with some very small dispersoids appearing in close proximity to larger dispersoids, something which is not seen in undeformed material.

![Backscattered images of longitudinal section 2C (a) low magnification (b) High magnification](image)

Figure 79 Backscattered images of longitudinal section 2C (a) low magnification (b) High magnification

Comparing the centre to the edge material shows how significant these differences are, the centre material appears identical to the post heat treated
material, while the edge material contains significantly more dispersoids, these appear rounder and very small particles are visible.

Figure 80 Backscattered images of transverse section; sample 2C (a) Centre (b) Edge
The particle size distribution, Figure 81, show a large increase in the density of particles greater than 50nm in size in the deformed material, notably there is no decrease in the density of smaller particles suggesting an evolution path other than pure coarsening.

Figure 81 Dispersoid effective radii sample 2C

Figure 82 Dispersoid aspect ratio distribution for sample 2C
The aspect ratio graph (Figure 82) shows that the shape distribution is significantly shifted towards rounder particles in deformed material, with the largest effect being in the transverse viewed effective radius sample.
**Sample 2D 10000 °s⁻¹**

This was the highest strain rate sample tested and actually reached the limits of the machines capability to accelerate to the required speed, this resulted in slightly irregular cycles of deformation. It is clear in the micrographs Figure 83 that the constituents have been aligned by the deformation, and that small new grains have been formed. Dispersoids appear rounded and many fine particles are observed. The grain structure has become very fine due to recrystalization and pinning.

![Micrographs of Sample 2D](image)

Figure 83 Backscattered images of longitudinal section, sample 2D (a) Low magnification (b) High magnification
The centre to edge comparison (Figure 84) is similar to the previous three, at the
centre dispersoids appear relatively similar to post heat treatment, while at the
edge they appear very rounded, and fine dispersoids are present, noticeably
these also appear in lines.

Figure 84 Backscattered images of transverse section; sample 2D (a) Centre (b) Edge
Figure 85 TEM image of edge material, sample 2D, showing dislocation structures around dispersoids

TEM imaging shows how the particles are rounded compared to those seen in the heat treated material (Figure 85), additionally dislocation structures can be seen surrounding and linking the dispersoids.

The size distribution shows that at the midpoint there is some possible nucleation occurring as the particle density is higher at small sizes, while at the edge there is some nucleation of smaller particles, along with a possible increase in the larger particles due to coarsening.
Aspect ratio distributions show that the effect is very strong in this sample, with a stronger effect in the mid and edge observations with less of a difference to the transverse view.

Figure 86 Dispersoid size distribution for sample 2D

Figure 87 Dispersoid aspect ratio distribution for sample 2D
Overall Statistics

Using image analysis to measure the particles as discussed in chapter 4, median values have been calculated for the particle populations. These figures for the dispersoids in these samples have been calculated. As seen in Figure 88 the median aspect ratio is seen to reduce across the samples in all samples, with the value at the centre being relatively close to that observed in heat treated material, while at the midpoint and edge it is reduced. Noticeably the measurements taken from the longitudinal sections (3.65mm) have the lowest values; this will be discussed further in relation to the distributions.

![Figure 88 Median particle aspect ratio for each position in torsion 2 samples](image)

The observed particle density is also seen to increase across samples, this is an unexpected result, as the expected response to high strain rate deformation was enhanced coarsening, which would slightly reduce the particle density as small dispersoids would be lost.
Examining the observed area fractions (Figure 90) suggests that the increased particle density is due to an actual increase in the amount of dispersoids in the material, rather than fracture of existing particles. Again the centre values are all close to the heat treated value, while effective radius and edge values are generally significantly increased. The mid values for 1000 and 100 are significantly far from a linear relationship, this is likely due to errors from oxidation and re-polishing these samples between microscope sessions.
The median particle radius (Figure 91) is slightly increased across the lower strain rate sample, suggesting that the dominant particle evolution mechanism has been coarsening, in the higher strain rate samples there has been little change, but as the area fraction and particle density has increased, this indicates that there must be a spreading of the dispersoid population distribution.
If the particle size distributions are plotted for the data taken from effective radius points, the populations can be assigned a true strain rate (Figure 92). The change in the distribution are now clearer, all of the deformed material shows an indication of coarsening, with a significant increase in the particle density between 50-90nm compared to the heat treated material. Additionally in the higher strain rate deformed materials there is an increase in the particle density in general, along with the shift, suggesting more particles have been formed.
The aspect ratio distributions of the effective radius samples show a large shift for all deformed samples. This is supported by the median particle aspect ratios (Figure 88). Notably the shift is not proportional to the strainrate.
4.3.3 Torsion 3 – Torsion testing at 450°C

The third round of torsion testing consisted of deformation tests at 100°s⁻¹ and 1000°s⁻¹ again for 100 180° cycles, but with the deformation performed at 450°C rather than at 500°C as before. This was done in order to examine the role of deformation on particle development where there was also undercooling introduced providing a driving force for additional precipitation. This experiment more closely mimics what happens during industrial processing, where the hot rolling temperature is below the homogenisation temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deformation rate (°s⁻¹)</th>
<th>Deformation angle (°)</th>
<th>Number of Cycles</th>
<th>Failed</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>100</td>
<td>180</td>
<td>100</td>
<td>No</td>
</tr>
<tr>
<td>3b</td>
<td>1000</td>
<td>180</td>
<td>100</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 6 Results of torsion tests at 450°C

Figure 94 Temperature and Deformation angle vs Time for Sample 3A
Figure 94 shows the temperature and deformation angle during the whole of the 100°s⁻¹ test. During deformation the temperature is again seen to slowly rise by around 1.5°C during the test, while the deformation cycles are very regular.

Figure 95 shows the torque and deformation angle of the sample during the 100°s⁻¹ test. While the Torque values are slightly higher for the lower temperature test, the shape of the torque curve is almost identical for the 100°s⁻¹ deformation rate samples.
Figure 96 Temperature vs Time for quenching of sample 3A

The cooling curve shows the samples was cooled to room temperature in less than 2 seconds, modifications were made to the machine between Torsion testing sets 2 and 3 aimed at improving the cooling system. The sharp change in cooling rate is likely due to the halting of the Leidenfrost effect on the sample surface, where there is a boundary layer of steam on the surface of the metal which reduces the heat transfer rate and therefore the cooling rate.
Sample 3a 100°s-1 180° 100 cycles

Figure 97 Backscattered SEM image of dispersoids in longitudinal section-Sample 3A

Figure 97 shows the microstructure of the material in the “effective radius” sample. Again the dispersoids are seen to be rounded, with fine dispersoids in the gaps between pre existing dispersoids. The grains observed are very small.
Figure 98 Backscattered images of transverse section sample 3A (a) Centre (b) Edge

The centre to edge comparison, Figure 98, shows an even larger difference to the samples deformed at 500°C, at the centre the dispersoid appear significantly larger, and considerably longer, as would be expected of semi coherent particles that have grown when the temperature has been lowered. At the edge, the dispersoids are much smaller, appearing as fine densely distributed spheres.

Figure 99 Dispersoid size distributions in sample 3A
Figure 99 shows the particle size distribution from image analysis, again these are significantly different; the mode value is significantly higher, representing the overall increase in particle size from pre existing particles that have grown. Additionally there is a slight secondary peak in each distribution towards the smaller end, representing newly nucleated particles; the distributions also show how the density of particles is much higher in deformed material.

The shape distributions (Figure 100) are significantly shifted with deformation, with many more particles in the 1-1.5 aspect ratio range in the centre and edge, again the strongest effect is seen in the longitudinally sectioned sample, but the reduction in aspect ratios above 1.8 is clear for all the deformed samples.
Sample 3B 1000°s-1 180° 100 cycles

The constituents look very similar to those found in sample 2C (Figure 101) which underwent the same deformation conditions, the dispersoids are rounded, and many fine particles are visible. A very fine deformation grain structure is visible, with dispersoids pinning the new grain boundaries.

Figure 101 Backscattered SEM images of transverse section, 3B (a) low magnification (b) High magnification

The centre edge comparison shows less of a difference than previous results, this is mainly due to a noticeable change in the centre material compared to the
centre of sample 2C. While large elongated particles are visible, there are many small particles, some of which appear in strings (Figure 102).

Figure 102 Backscattered images of transverse section sample 3B (a) Centre (b) Edge
The particle distribution statistics show another increase in particles for the deformed material. The mode particle size is slightly smaller for this sample compared to sample 2 and there are many more particles in the 20-40nm radius range for the deformed areas.

The aspect ratios show another typical shift towards the 1-1.6 range, and that the centre particle distribution has also shifted unlike for the lower strain rate sample.
Particle Statistics

As with the results of the torsion tests performed at 500°C, overall statistics for the particle populations in the samples deformed at 450°C.

The particle density is seen to increase across these samples, this relationship is clear in both samples unlike in the isothermal deformation samples; however the increase is almost identical in both samples deformed at 1000s⁻¹.
Figure 106 shows the median particle radius across the samples. This shows that the particle radius is considerably lower in the longitudinal sections. There is a trend towards smaller particles across the samples, suggesting there are more, smaller particles in the more deformed material. The median radius is notably lower for the transverse viewed sample (3.35mm) which is probably due to a larger alignment effect with the larger particles that are being formed.
The area fraction graphs again show an anomalous result for the transverse view points, while the sectioned samples show a small increase for the slower strain rate with increased deformation, while for the higher strain rate sample it is almost constant. This suggests that for the lower strain rate material the increase deformation is increasing the amount of phase precipitated across the sample, while for the higher strain rate sample the increase is simply increasing the number of particles.

The median aspect ratios are slightly reduced across these samples. Notably the median aspect ratio for the undeformed material at the centre of the 100°s⁻¹ sample is higher than in the post heat treatment material, demonstrating that the particles have grown in one direction preferentially. While the median aspect ratio for the centre of the 1000°s⁻¹ sample is slightly lower.
The longitudinally sectioned (3.65mm) points fit well with the results from the transverse sectioned samples, and match very closely to the results of the 500°C deformation experiments.

Figure 108 Median particle aspect ratio across torsion 3 samples
Chapter 5-Discussion

This chapter discusses the results given in chapter 5, and compares the results of different experiments to one another, and place the experiments in the context of existing work.

5.1 Initial post heat treatment microstructures

The post heat treatment microstructure is very similar to what would be expected from reviewing the literature (Li & Arnberg 2003)(Dehmas et al. 2012)(Li et al. 2012). It contains large constituent particles and fine dispersoids, non-uniformly distributed within the grains. The mean effective radius of the dispersoids is around 50nm, and there is around a 1.2% observed area fraction of these particles. High resolution SEM and TEM images show the dispersoids have straight edges and square corners as seen in other works. It can therefore be assumed that these particles are representative of those found in this type of alloy both in the literature, and those found in commercially produced material, which have been characterised in previous works (Du et al. 2013)(Anselmino et al. 2004).

5.2 Aspect Ratio Changes

As shown in the results, the mean aspect ratio of particle is seen to decrease with increasing deformation when making observations across a sample (Figure 88). More significantly the aspect ratio distributions are seen to be shifted after deformation, with many more particles having a low aspect ratio. A large effect is seen in all samples. The change in aspect ratios is evidence that the particles have become closer to spherical in shape, rather than the elongated rectangles seen in the heat treated material.
If the measurements taken at the effective radius in the transverse view samples are compared to the heat treated material (Figure 93) it can be seen there is another shift towards lower aspect ratios, with aspect ratios of less than 1.4 being far more common in the deformed material, making up over 50% of particles compared to only 20% in heat treated material.

Conversely aspect ratios over 2 are far more prominent in heat treated material making up 35% of particles, while making up less than 15% in deformed material. While for the samples deformed at deformation rates of 100°s⁻¹ 500°s⁻¹ and 1000°s⁻¹ these effects seem to be strain rate dependent, the 10000°s⁻¹ data suggests that this is not the case as there is a smaller effect in the highest strain rate sample. This is not the case if the same comparisons are made in the centre to edge samples, where the effect is always strongest towards the edge, suggesting that cumulative strain is also having an effect on the amount of spheroidization, though as both strain and strain rate vary together it is not possible to separate the effects using this data.

For 100°s⁻¹, 500°s⁻¹ and 1000°s⁻¹ samples there is a significant increase in aspect ratio shift in the “effective radius” samples compared to the edge material. Referring back to section 3.4 it can be seen that the edge material will have received a higher cumulative strain and strain rate than the material imaged in the “effective radius” section; this is also seen in a lowest mean aspect ratio measurement for the effective radius material. This is likely due to some alignment of the particles due to deformation, creating an additional shift in aspect ratio in the “effective radius” sample in which the axis of the image is at 90° to the deformation axis, instead of in line.

For the highest strain rate sample this is not seen, and the mean aspect ratio is relatively similar across the sample, however it is reduced in all positions compared to the heat treated material. For the this sample, the closeness of the
results from centre to edge, and the slightly less than expected reduction in mean may all be due to the issue experienced during the test discussed previously. At this high strain rate, cracks appeared in the edge of the samples, penetrating inwards. This was not enough to cause sample failure, as seen in previous tests, but is may have reduced the amount of strain experienced by the edge material if the cracks allowed slip between the two surfaces. Cracking at high temperatures and high strain rates has been seen in similar materials and has been attributed cleavage fracture due to melting at grain boundaries (Deschamps et al. 2002). This process would not have altered the deformation in uncracked areas, as the test was position controlled and fixed geometry of the test setup will not allow non-uniform deformation. This could explain why the results are more closely grouped than the other samples, but are not the lowest values measures, as would be expected if it was simply the limit of possible change that had been reached.

When the changes in distribution from centre to edge are compared for the three lower strain rate samples, the magnitude of the shift does appear to correlate with strain rate, with the change in the curve for the population at the mid radius point of the sample shifting significantly more with faster deformation. This suggests that this process is both strain and strain rate dependant, and therefore linked to the deformation mechanisms.

5.2.2 Size Split comparisons

In order to separate the aspect ratio change from the effect of any new particle nucleation the aspect ratio plots have been split, with particles above and below the median radius plotted as separate curves. If the shift in particle shape is due to an increase in small spherical particles these curves will be significantly different, with the larger than average particle curve unchanged.
As would be expected there is some difference in the aspect ratio between the small and large heat treated material curves (Figure 109), this is due to the fact that larger particles will tend to have a larger aspect ratio as the growth occurs far more in one direction. The small particle population consists of both particles that have undergone limited growth so have remained more equiaxed, as well as larger particles imaged in cross section. In both cases a lower aspect ratio (closer to 1) is expected, as observed.

When the data from torsion tests is plotted in the same way, Figure 110 and Figure 111, the difference between large and small particles is much smaller; both curves have been shifted towards lower aspect ratios. For the 100°s⁻¹ sample the curves are almost identical, suggesting that all particles have been affected in this way. In the 1000°s⁻¹ case the effect is slightly stronger in small particles, suggesting there is some input from the nucleation of small particles, however there is still a major shift in the distribution of large particles indicating that a shape change occurs in all sizes of particles.
The particle distribution change can also be visualised using intensity plots; these show the number density of particles of a particular size and aspect ratio via colours. The X axis of the plots shows the aspect ratios, while the Y axis
shows the effective particle radius. The purpose of these plots is to more clearly visualise the changes in aspect ratio with particle size between specimens.

Figure 112 Intensity plot of Aspect ratio vs. particle size (heat treated material)

The heat treated results, Figure 112, show a wide spread of aspect ratios, with the main concentrations of particles at aspect ratios below 2, but a significant spread especially at larger sizes. Size concentrations are also spread out, with the highest frequency occurring for small particles with aspect ratios of about 1.5 and 2.

Figure 113 Particle intensity distribution (Sample 2A)
The 100°s\(^{-1}\) deformed material has a much smaller spread in aspect ratios, seen in Figure 113, the shift towards aspect ratios less than 1.5 can be seen for all sizes of particle, it can also be seen that the sizes of particle are concentrated in the range of 30-50nm although larger particles exist in relatively high numbers.

![Intensity plot of aspect ratio vs particle effective radius (sample 2C)](image)

Figure 114 Intensity plot of aspect ratio vs particle effective radius (sample 2C)

The results of the higher deformation rate tests, Figure 114 and Figure 115, are similar, it can be seen that the spread of particles is reduced in the deformed material, and that in the highest strain rate sample they are concentrated in the 1-1.3 aspect ratio range. Meanwhile there is a shift of the main concentration of particles towards slightly larger sizes (<50nm towards 50-70nm) with increased deformation rates. Particles nucleated during the deformation appear as intensity spots at small sizes (~20\(\mu\)m radius), with an aspect ratio of around 1.25.
To understand the reason for particle shape changes it is necessary to understand the reason for the particles shape to begin with. As discussed in chapter 2, the dispersoid particles are formed of the α-Al-(Fe,Mn)-Si phase, which has a cubic structure and forms a semi-coherent interface with the aluminium matrix (Li et al. 2012). Because of this, the expansion of the coherent side has a relatively low energy, and the surface has a low mobility. Therefore the particles grow in length (perpendicular to the coherent interface) outwards while remaining close to the same thickness. This results in the straight edged, sharp cornered dispersoids seen in the TEM image (Figure 48). This shape is stable (gives the lowest overall interfacial energy) provided that the surfaces remain in their coherent state.

If the influence of deformation is considered, there are several effects which could alter the particles. Firstly larger particles could be broken up by the deformation processes, however this would result in a loss of larger particles along with an increase in smaller particles. This is not seen in this data, and is also unsupported by the larger round particles seen in the micrographs, and the lack of observation of any fractured dispersoids.
Instead, the interaction of deformation induced defects with the particles, and particularly on the interfacial properties of the dispersoids, must be considered. As discussed in chapter 2, when deformation occurs, the dislocation density of the material is greatly increased. These dislocations move through the material, and their interaction with one another produce jogs. These can then produce vacancies which are also mobile. If the dislocations hit a dispersoid they are stopped, as they cannot continue through the lattice of the particle. This leads to dislocations building up on the surface of the dispersoid. As the sides with the coherent interface are the longest, they will be the ones that dislocations interact with the most. This can be seen in the TEM images of deformed material Figure 116 in which dislocation networks can be seen emanating from the surface of the particles.

Figure 116 Brightfield TEM image of dislocation network around a dispersoid
(Sample 2D)(100kV objective aperture)

While the semi coherent interface will have some naturally occurring dislocation in order to allow for the slight misfit, a large increase in the number of dislocations on the surface will break down the coherency of the interface. At this point, the surface energy of the dispersoid will be significantly increased. Additionally the mobility of the surface will be increased by the distortion of
the lattice and the presence of dislocations and possibly vacancies nearby. This results in a situation in which the driving force for spheroidization is increased, from the increase in surface energy, and the diffusion kinetics required for this process to occur are also enhanced. Therefore the particles will tend to reduce in surface area, losing their elongated shape and becoming more rounded. This accounts for the drastic shifts in aspect ratio distributions seen, but would not significantly alter the measured areas of the particles, from which the effective size has been calculated. The high magnification images show that the dispersoid do have a rounded shape, and have lost the sharp corners seen previously, this also agrees with the theory that the dispersoids are spheroidizing. This type of coherency loss is usually seen during the growth of particles when the radius reaches a critical value at which the misfit strain cannot be accommodated, (Iwamura & Miura 2004). However mechanisms for the loss of coherency such as dislocation wrap-around have been proposed as possible in deformed material (D A Porter & Easterling 1996). Similar coherency loss has been seen in Al₃(Sc,Zr) precipitates in material that has been subjected to similar high strain rate deformation during equal angle channel pressing (Schöbel et al. 2012), these particles were smaller, and while a shape change was not found, particle break up and a slight rotation occurred. This slight rotation could account for the increased aspect ratio shift seen in the transverse samples compared to the axial centre to edge samples. Particles in Al-Sc alloys have also been found to change from coherent to semi-coherent after low angle grain boundaries passed the particles(Jones & Humphreys 2003).

The effect of particle shape change on the surface area to volume ratio can be calculated using simple geometry. If the typical mean particle statistics from heat treated material are used, and a cuboid particle is assumed, an aspect ratio of 1.94 and an observed area of 0.16µm² give a surface area/volume of 53.67µm⁻¹. A similar particle with an aspect ratio of 1.44 as found in the 1.8s⁻¹ material has surface area/volume of 53.2µm⁻¹, a difference which is insignificant;
however the particles do not only change in aspect ratio, but in overall shape. If instead the particles are modelled as spheroids, as the particles observed in the material appear after deformation, this ratio is reduced to 43.2µm⁻¹, a difference of almost 20%, this compares to 42.24 µm⁻¹ for a perfectly spherical particle of the same volume. This means that by becoming spherodial and slightly reducing their aspect ratios, the particles significantly reduce the interfacial area required, and hence total surface energy (assuming this becomes nearly isotropic after coherency loss) to produce a large reduction in surface area. Therefore it is clear that the particles do not need to become perfectly spherical, and the observed changes fit with the theory that shape change is due to increased interfacial energy and coherency loss, meaning the large flat initially low energy faces lose their energy advantage.

As discussed, the loss of coherency of a particle will result in an increased surface energy, promoting both the reduction in surface area, but also an enhanced drive for coarsening. This is also seen in particles which go through a coherent stage of development during growth. Once particles reach a critical size threshold coherency is lost due to increasing misfit strain, this increases the driving force for coarsening and so enhances the particle coarsening rate.
5.3 Particle Size change

As discussed in chapter 3, the expected outcome of the experiments was enhanced coarsening of the dispersoids. This would be due to the increased diffusion rates caused by enhanced vacancy concentrations within the matrix, and pipe diffusion along the cores of dislocations. The coarsening rates should also be enhanced by any change in dispersoid-matrix interface as is seen in other systems when particles loose coherency (Iwamura & Miura 2004). Enhanced coarsening would appear as a shift towards larger particles, and a slight reduction in particle density. A comparison of results from different strain rate experiments is shown in Figure 117. This figure is normalised to the area number density of the particles.

The area normalised data can be difficult to interpret due to the overall increase in particle density seen in the higher strain rate material, and the differences between samples caused by slight differences in preparation. However the plots can instead be normalised for particle fraction, as has been done for aspect ratios. When this is done for the effective radius results, there is a significant
difference. The heat treated material has a large peak of particles smaller than 30nm in radius, whereas for the material deformed at 0.9s\(^{-1}\) and 1.8s\(^{-1}\) there is a smaller peak at this size, and the curve is flattened out over the 30-50nm radius range. This could be simply from heating effects, but as the change in the curve is even larger for the 18s\(^{-1}\) peak, with the peak size being 30-40nm and the fraction of particles somewhat higher above 60nm, there seems to be considerable evidence that coarsening has taken place, and that this coarsening has been influenced by the strain rate.

![Figure 118 Particle sizes normalised for number of particles (longitudinal samples)](image)

Plotting a comparison of edge particles also allows a comparison to be made, while the exact strain rate cannot be easily calculated, taking results from the same point in each sample allows qualitative comparison to be made. The three samples given here had an order of magnitude increase strain rate.
Figure 119 Particle size distributions (Torsion 2 edge material)

The area normalised results (Figure 119) do show a significant change in the curves, but the influence of new particles shifts the curves for the deformed material upwards, meaning that the change in size distribution is masked.

Normalising for the number of particles (Figure 120) shows a shift towards larger particle sizes for all of the deformed material; the clearest difference is in the fraction of particles below 40nm, where the edge material has 20% fewer particles below this size, while there is an increase in particles above 70nm in the deformed material.
Figure 120 Number normalized particle sizes (heat treated and edge of sample for 2A, 2C, 2D)

Additionally when the intensity plots are examined there is a clear shift in the vertical location of the highest concentration of particles, indicating that while new particles may have formed, and the mean radius therefore decreased, there has been some growth of the pre-existing particles.

The level of coarsening seen at the higher strain rate is similar to that seen for around a 1 hour hold in previous works, (Li & Arnberg 2003). The rate of coarsening has therefore increased by around an order of magnitude. This is similar to the enhancement of coarsening seen by other work examining deformation effects on coarsening (Deschamps et al. 2012)

This enhanced coarsening effect can be attributed to several factors, all of which may take a role in the process. Firstly, as initially thought the deformation processes create a super saturation of dislocation jogs and vacancies that will enhance diffusion. This would be a strain-rate dependant process, and so the
evidence seen here suggests this is most likely to be the major factor, as the change seems strain rate dependent. Secondly, the breakdown of the semi coherency of the particles would also increase the driving force for coarsening.

Additionally a third factor may be involved. In the deformed material an increase in both the number density, and the observed area fraction was seen, this suggests that there was some supersaturation (e.g. of Mn) which was encouraged to precipitate by the action of deformation. In addition to forming new particles, this could lead to further growth of existing particles.
5.4 Nucleation enhancement in deformed material

The measured particle densities clearly increased across three of the samples (Figure 89), with the only exception being in the lowest strain rate sample. This trend is also seen in the effective radius samples, apart from the $1000\text{s}^{-1}$ sample (Figure 121).

Figure 121 Particle density with strain rate (Torsion 2 effective radius samples)

Figure 122 Backscattered SEM image of sample 2C (longitudinal specimen, nucleated particles highlighted)
Figure 123 (a,b) Backscattered SEM image of sample 2C (longitudinal specimen, nucleated particles expanded)
Figure 124 Backscattered SEM image of sample 2C (longitudinal specimen, nucleated particles highlighted)
Perhaps the most significant, and certainly the most unexpected observation in this work is that there was an increased number of small particles in deformed material. Small, round dispersoid particles are visible in many of the SEM images taken of deformed material; these have been highlighted with yellow ovals. There are several reasons to believe these are new particles from observation alone. Firstly, similar particles are not observed in heat treated material. Secondly their size suggests that they would have been removed via coarsening during the preceding heat treatments as they are much smaller than the observed post heat treatment particles. Thirdly they are often observed in very close proximity to one another, and in lines of 3 or 4, this suggest that they have precipitated recently, and that precipitation has occurred on a deformation structure.

This is supported by the statistical data, which shows an increase in the number of small particles in the deformed material. This is accompanied by an observed increase in the overall number density of the particles and the observed area fraction. The increase in area fraction is important, as this demonstrates that the small particles are new entities, and not pre existing dispersoids which have
fractured during high strain rate deformation. Additionally the particle distribution graphs of samples in chapter 4 clearly show that the pre existing particles remain.

This result runs counter to what would usually be expected, as new nucleation is unlikely in material which should be at equilibrium, as both conductivity measurements and mathematical analysis show that all super saturation of manganese should have been removed during the previous heat treatment. Conductivity measurements showed no increased in conductivity after 2 hours at 500, and a calculation of the diffusion distance for this time gives a distance of 0.62µm, enough to remove manganese from all of the inter-dispersoid spaces.

To explain this result, the interaction of the manganese remaining in solution and the dislocations must be considered. It has previously been demonstrated that dislocations are the nucleation sites for dispersoid particles in these alloys (Chen et al. 2003), and that deformation of a super saturated material leads to precipitation of fine dispersoids, due to a large increase in the number of nucleation sites.

The nucleation of dispersoids on dislocations is likely as the strain field around the dislocation effectively removes the misfit strain of the nuclei, and thus lowers the energy barrier required for nucleation (Cahn 1957; Cahn 1960)(Christian 1965). By removing the elastic strain energy for nucleation, the energy barrier is only due to the surface energy and this is relatively low if the surfaces have coherency with the matrix. The difficulty in producing a fine dispersoid population in undeformed material is testament to the difficulty in overcoming the energy barrier to nucleation then strain is present, as rapid temperature drops or extended holds are required for nucleation.

While the source of new particle nucleation sites is easily attributed to the increase in available dislocations, as the dislocation density will be several
orders of magnitude higher during deformation, the cause of the necessary
driving force is more complicated. Without a driving force from thermal effects,
the new nucleation must be a result of either a localized supersaturation, with
manganese concentrations being greatly increased on the micro scale, or an
overall reduction in the effective solubility.

Microsegregation could be occurring due to segregation effects due to solute
sweep, where solute atoms are segregated to areas around dislocations. The
idea of a “solute atmosphere” around a dislocation was first proposed by
Cotrell (Cottrell & Bilby 1949) this suggests that the solute is more concentrated
close to dislocations, as the strain field created by the dislocation cancels out the
misfit strain of the solute atom. In the case of manganese the misfit is
considerable, as the atomic radius of manganese is 5% smaller than an
aluminium atom; this will result in a higher concentration of manganese around
dislocations. These solute atoms also act as a drag force on the movement of
dislocations (Yoshinaga & Morozumi 1971) When the dislocations then move
through the material, they can “sweep” up the solute in the material, when
dislocations then interact this will create a nucleation site, surrounded by an
increased concentration of solute, and enhanced diffusion pathways. These
processes may well combine to create a situation in which nucleation can occur,
for example a higher than equilibrium solute concentration in the local volume
around a dislocation could be triggered to nucleate a dispersoid by an
interaction with another dislocation. Segregation of solute to dislocations and
vacancies has theoretical and experimental basis, and has been shown to reduce
the Gibbs energy of these defects (Kirchheim 2007b; Kirchheim 2007a).
Microsegregation due to the dislocation networks formed during cold working
has been attributed to altering the nucleation kinetics in similar material (Chen
et al. 2003), however as this work investigated cold rolling followed by
annealing, concurrent precipitation did not occur, and the dislocation density
was reduced before precipitation started. Therefore this work would not have observed an increase in particle number density.

Another possibility is that the additional stored energy within the lattice due to the very high level of defects created by this deformation may itself reduce the effective solubility of manganese by effectively destabilising the matrix, thus creating a driving force for nucleation. Combined with the increased surface energy of the existing particles, reducing the driving force for growth, and the very high number of nucleation sites due to the high dislocation density, this could account for how new particle nucleation could occur, and accounts for the observed particle density and area fraction increase. This is supported by the observations of fine dispersoids appearing between other larger dispersoids, and sometimes appearing in lines, as if nucleated along a dislocation or cell wall.

While nucleation and growth of the particles under non equilibrium conditions due to deformation may be contentious, there are parallels with other systems in which non equilibrium processes occur. It has been found that in material subjected to neutron irradiation, segregation and precipitates form that would not be expected when only accounting for the thermal equilibrium. These have been attributed to the effect of neutrons creating defects, such as vacancies, and increasing the energy of the matrix. This is similar to the process seen here, where the increased number of crystallographic flaws stems from the high strain rate of the deformation. This process has been observed and accounted for in steels irradiated at temperature where carbides are formed. Investigations into these phenomena have revealed microsegregation of alloying elements within the material, along with non-thermal equilibrium phase formation (Maziasz 1989) These irradiation enhanced process can lead to undesired effects such as irradiation induced sensitisation in stainless steels.
In irradiated material this process is usually referred to as radiation induced segregation, and can result in levels of segregation sufficient to cause failures of components due to loss of passivation (Zinkle & Was 2013). The mechanisms that result in this are now well understood, and have been the subject of considerable work. The process is attributed to the inverse Kirkendall effect (Marwick 1978), whereby the creation of vacancies by irradiation damage leads to an enhanced vacancy concentration, and a resulting flux of vacancies towards sinks (such as grain boundaries and dislocations). This flux of vacancies requires a corresponding flux of matrix atoms in the opposite direction, as the faster diffusing species will diffuse more readily by this process; a concentration gradient is created, with faster diffusing species being depleted near sinks, and slower diffusing species being enriched. During deformation of material discussed in this work this process could result in an enhancement of manganese at dislocation tangles, which would act as sinks, allowing a high enough enrichment to result in nucleation of particles.

It is worth considering that the material observed here was cooled very rapidly at the end of deformation, and so the increase in particle fraction may well disappear if the particles are unstable and dissolve if the material was held at temperature at the end of deformation, along with the associated increase in particle number density. In reality though material deformed in commercial processes is constantly cooling while deformation is ongoing, therefore the newly nucleated particles may continue to grow as the temperature decreases.
5.5 Lower Temperature Torsion

Lower temperature torsion tests were planned after obtaining the initial results from the second round of torsion tests. The idea behind these experiments was to examine how deformation altered the particle development under conditions closer to those seen in actual processing, where the rolling temperature used are less than the prior homogenisation temperature. In commercial rolling, the temperature varies as the billet cools between rolling passes, is then heated by the deformation process, and then cools again. However in order to be able to make some comparisons in the present study the temperature was kept constant for the tests at 450°C.

Again the deformation temperature varied only slightly during the experiments, with a gradual increase in temperature during the tests. As would be expected, the torque required for deformation was slightly higher for the same deformation rate, due to the lower temperature. However the shape of the torque curve (Figure 95) is very similar for the same deformation rate between the two experiments.

The particle density is seen to increase across the samples (Figure 105), with a significant increase in the deformed material towards the edge. More significantly, the mean radii are drastically reduced in deformed material compared to the undeformed, with the size of the decrease increasing with strainrate. The area fraction increases across the lower strainrate sample, however it is relatively constant in the higher strain rate sample, although at a high level for all measurements. This suggests that deformation triggers new particle nucleation, rather than the growth of pre-existing particles, when there is a thermally created supersaturation of manganese. This agrees with the previous work that has found deformation of material followed by a temperature drop produces finer particle dispersions due to the increase in available nucleation sites.
The particle distribution curves reflect this (Figure 99, Figure 103), in the centre material in sample 3B there is a very flat particle distribution, indicating that pre-existing particles have grown, this is supported by the large mean particle radius, the highest of any sample, and the relatively low particle density, which is around the same as the centre of the low strain rate torsion 2 samples (2A/B). It is clear that precipitation has not occurred to any great extent; interestingly this also results in a lower observed area fraction than in the deformed parts of this sample, likely because the diffusion rate is not high enough for the supersaturated manganese to travel from the centre of the inter-dispersoid spaces to the pre-existing particles during the time at 450°C. In the curves for the deformed areas there is a clear increase in particles between 40-150nm in radius, while the observed area fraction is over 25% higher, indicating that nucleation has allowed not only an increase in particle density, but an increased volume fraction of dispersoids as the solute atoms have formed new particles rather than being required to diffuse across a inter-dispersoid gap. The increase in dispersoid density is clearly evident in the micrographs of this material, seen in Figure 98.

In the higher strain rate sample the increase in particle density across the sample is still present, while the reduction in mean particle radius is more pronounced. However, at the centre point there has still been an increase in the area fraction, along with a higher particle density than seen in the isothermal tests. This suggests that while the centre point of the lower strainrate sample has been relatively unaffected by deformation, the centre of this sample has been affected by the deformation mechanisms. This is likely due to the increased dislocation density due to deformation at lower temperatures, due to the reduction in flow stress, allowing some new nucleation, as only the exact centre of the sample (at the axis) will be completely undeformed. The particle distribution curves support this, with the centre curve being less flattened than for the lowest strain rate sample. There is still a clear increase in particles
between 40nm and 100nm in radii in the mid radius and edge material, suggesting that the nucleation was enhanced further by the deformation mechanisms. There was little change in observed area fraction however, suggesting that above a certain point increasing the available nucleation sites only increases particle density and reduces mean radius, as the volume fraction has reached a limit. Notably the increase in volume fraction for all deformed material is higher than would be expected by a thermal calculation alone. Figure 36 plot when compare to the isothermal tests, suggesting that the previously observed increase due to deformation is also having an effect.

The aspect ratio changes for the lower strain rate sample fit closely with those observed in the previous tests, notably the centre material has the highest measure mean aspect ratio, fitting with the large, elongated particles seen in the micrographs. In the deformed material the mean is lower and the population is shifted towards lower aspect ratios, with the majority of particles below an aspect ratio of 1.5. Again the largest shift is seen in the transverse images. In the highest strain rate sample, a large shift is seen in all parts of the sample, with the mean also reduced. This shift in the centre fits with the observed changes in particle size and density, and again suggests that in the centre of this material, deformation mechanisms have still played a role in particle development, despite the very low strain. This is also supported by the micrographs, which show rounded particle in both the centre and edge of the material. Similar effects were seen in sample F of the Torsion 2 experiments, which experienced the highest strain rate of any material.

In all it is clear that for material deformed below the final heat treatment temperature, the role of deformation mechanisms is significant. Compared to material that is not deformed, the dispersoids will be smaller, with higher number density and more rounded in shape with an increased volume fraction created in a short period of time. These factors will all make a significant change
to the effects the population has on the material properties, and could significantly alter the effect of dispersoids on further microstructural evolution during downstream processing. The significance of these changes can be calculated using Zener pinning theory.

5.6 Effect on Zener pinning pressure

The effect of the changes to the dispersoid particles can be calculated as the Zener pinning pressure of a dispersoid population is proportional to the volume fraction and inversely proportional to the mean particle size (Nes 1976) (N Sun et al. 2006).

\[
\text{Pinning Pressure} \propto \frac{\text{Volume Fraction}}{\text{Mean Radius}}
\]

A relative particle pinning pressure can be calculated for each of the conditions examined in this work. If the particle pinning pressure of the post homogenisation population is defined as 1. For the material deformed at 0.9s\(^{-1}\) the relative pinning pressure is increased to 1.225. For the 18s\(^{-1}\) material this is increased further to 1.409. This represents over a 40% increase in the Zener pinning pressure compared to that which would be expected from the original microstructure. A larger pinning pressure will result in a smaller grain size after recrystalization. This can be estimated using the Zener limited grain size calculation (Humphreys & Hatherly 2004), where the limiting grain size \(D_{\text{Zener}}\) is calculated according to:

\[
D_{\text{Zener}} = \frac{4r}{3Fv}
\]
Where \( r \) is the mean particle radius and \( F_v \) the volume fraction of dispersoids. For the post heat treatment grain size this gives a grain size of 5.82\( \mu \)m, for the 0.18\( s^{-1} \) material this is reduced to 5.06\( \mu \)m and for the 18\( s^{-1} \) material 4.15\( \mu \)m. For the edge material deformed at 1000\( ^\circ \)s\(^{-1} \) at 450\( ^\circ \)C this is reduced to below 3\( \mu \)m. These numbers match the general observations of small grains (3–10\( \mu \)m) in the deformed material.

This could be influential on the downstream processing of material, possibly allowing a lower level of alloying elements to be added to the material in order to produce dispersoids. It is also worth noting that the shape of dispersoids has an effect on the Zener pinning potential of a particle population, and the shape change shown in this work may have an additional strengthening effect on the Zener pinning potential (Li & Easterling 1990).
Chapter 6-Modelling

Part of the scope of the project was to develop a constitutive model based on previous works that would calculate the effect of deformation processing on the resulting microstructure. This took the form of adapting and developing two previous models developed for steels. The development and testing of these models is discussed in this chapter.

6.1 Diffusion Modelling

The first part of creating a model for the project was the development of a physically based model that can allow the influence of different deformation mechanisms to be calculated from the processing parameters. To do this, the model first developed by Militzer, Sun and Jonas (Militzer et al. 1994) has been recreated, with modifications to make the model suitable for aluminium rather than the steel for which it was originally intended. The model calculates an enhancement due to diffusion from a combination of both enhanced vacancy concentration, and pipe diffusion along dislocations.

The model has been created as a function in MATLAB and requires a large number of constants; the values these are given. A breakdown and explanation of the model and the origin of the constants used for the calculations is presented below.

6.1.1 The model

The first step is the calculation of the realistic shear modulus of aluminium which is a function of temperature; this comes from the linear relationship predicted by Jmat pro. The shear modulus is required as it is a key parameter in determining the energy of a dislocation.

\[ \mu = U \left( 1 - \frac{U_t(T - 300)}{930} \right) \]
Where $\mu$ is the shear modulus at temperature, $T$ the temperature in Kelvin, $U_t$ a constant set to 0.6, and $U$ the shear modulus at room temperature, calculated in Jmat pro as $2.43 \times 10^{10}$ MPa. Next the jog formation energy is calculated;

\[
E_j = \frac{\mu b^3}{4\pi(1 - \nu)}
\]

Where $E_j$ is the jog formation energy for aluminium, $b$ the burgers vector, set to $2.86 \times 10^{-10}$ m (Totten 2003), and $\nu$ the poisons ratio, set to 0.33. This can then be used to calculate the concentration of thermal jogs at temperature.

\[
c_j = e^{-\frac{E_j}{kT}}
\]

Where $c_j$ is the jog concentration, $T$ the temperature in Kelvin and $k$ the boltzman constant set to 1.381 (Podesta et al. 2013). The next step is to calculate the neutralisation parameter, which accounts for the neutralization effect by vacancy emitting and absorbing jogs. This parameter effectively reduces the vacancies generated by a scaling factor varied between 0 and 1. If the value of $c_j < 0.036$, then the parameter followed the equation:

\[
\zeta = 0.5 - (\zeta_0 * c_j)
\]

Where $\zeta$ is the neutralisation parameter and $\zeta_0$ the input value, set here to be 0.5. Otherwise the neutralisation factor was set to 0.
The next step is to include a time variable, where \( t \) is the total time, \( t_d \) the deformation time and \( t_r \) the recovery time, this allows the time dependence of the vacancy concentration to be determined when deformation is stopped. This is particular importance when there are multiple deformation steps with pauses in-between.

\[
t = t_d + t_r
\]

As later steps require the calculation the dislocation density of the material it is necessary to know the stress within the material. Rather than the method used by Militzer the flow stress was calculated from strain rate and temperature, a standard constitutive equation for aluminium alloy was used, with the constants taken from (Tello et al. 2010):

\[
Z = \varepsilon^\dot{\varepsilon} e^{\frac{Q_{ZH}}{n}}
\]

\[
x_{ZH} = \left( \frac{Z}{A_{ZH}} \right)^{1/n}
\]

\[
\sigma = 1 \times 10^6 \frac{1}{\alpha} \text{asinh}(X_{ZH})
\]

Where \( Q_{ZH}, n, A_{ZH} \) and \( \alpha \) are deformation constants specific to the alloy, and are available in the literature from work on deformation processing (Tello et al. 2010) (set here \( Q_{ZH} = 134158, n = 3.246, A_{ZH} = 1.259 \times 10^8 \alpha = 0.0306 \)). \( R \) is the molar gas constant. \( \varepsilon^\dot{\varepsilon} \) is the strain rate, which is a model input.

The relationship between strainrate, stress and temperature predicted is given in Figure 126.
The dislocation density is then calculated using a modification of the equation used by Militzer, the equation for geometrically necessary dislocations is adjusted to be more accurate for aluminium.

\[ \rho_s = \left( \frac{\sigma}{ab\mu} \right)^2 \]

Here \( \rho_s \) is the dislocation density and \( \alpha \) a constant set to 0.6. However the dislocation density is also time dependent during the initial stages of deformation until a steady state is reached, and determined by an exponential relationship related to the characteristic time \( \beta \).

\[ \beta = \sigma \beta_0 \]

\[ pt = ps - (ps - p_0)e^{-\frac{\tau d}{\beta}} \]
Where $\beta_0$ is a material constant (set here to $5 \times 10^8$ based on the value used by Militzer) and $\rho_0$ the dislocation density of the material before deformation set to $10^{10}$.

This then gives enough information to calculate the production rate of excess vacancies within the material.

$$\Pi = \left( \chi \left( \frac{\sigma \Omega}{Q_f} \right) \varepsilon^* \right) + \zeta \left( \frac{c j \Omega}{4 b^3} \right) \varepsilon^*$$

Where $\varepsilon^*$ is the strain rate, $\sigma$ the stress, $\chi$ is a mechanical constant, set as 0.1, $\Omega$ is the atomic volume, calculated as $1.22 \times 10^{-29}$, $Q_f$ the vacancy formation energy, and $\Pi$ is the vacancy production rate.

The next step of the model is a calculation of the steady state vacancy concentration for the strain rate, this is a complex equation

$$C_s = \frac{K^2 \rho^2 \Omega_0}{D_v} A^n \exp \left\{ - \frac{Q_{def}}{nkT} \right\} \times \left[ \frac{X b^2}{Q_f} \varepsilon^{(1-\frac{1}{n})} + \frac{\zeta c_j}{4b} A^n \exp \left\{ - \frac{Q_{def}}{nkT} \right\} \varepsilon^{(1-\frac{\zeta}{n})} \right]$$

Where $K$ is a constant describing the dislocation structure, Militzer used $K=1$ for a homogenous dislocation structure and 10 for a cell like structure, for this work it was left at 1. $C_s$ is the steady state vacancy concentration; this is then adjusted for the changes which occur during the deformation of the material, namely the increase in dislocation density which requires a short time to reach the constant value.

$$C_{ext} = C_s \left( 1 - e^{-D_{v}\frac{\varepsilon t}{kT} + \frac{L_{ext}}{x} t} \right)$$
Where $L$ is the grain size, experimentally measured as 0.0001 m for the initial material. This equation calculates the excess vacancy concentration $C_{ext}$ at a specific deformation time; this is then modified to include time for recovery:

$$C_{ex} = C_{exd} e^{-D_v \left( \frac{\nu_1}{\nu + 1} \right) t}$$

To calculate the increase in diffusion, this excess vacancy concentration needs to be compared to the thermal vacancy concentration, in pure aluminium this is given as:

$$C_{th} = 23 e^{-\frac{63700}{RT}}$$

The annihilation of vacancies is a diffusion controlled process, as vacancy annihilation takes place at particular sites, thus the thermal diffusion rate of vacancies must be calculated using the usual exponential relationship.

$$D_v = D_{vo} e^{-\frac{Q_m}{kT}}$$

Where $Q_m$ is the vacancy migration energy, set as $1.04 \times 10^{-19}$ and $D_{vo}$ is the vacancy diffusivity constant set as 0.019. The annihilation rate of vacancies can then be calculated as the rate at which vacancies encounter grain boundaries and dislocations;

$$\eta = \frac{D_v \nu_1}{K^2} C_{ex} + \frac{D_v}{L^2} C_{ex}$$

The excess vacancy production rate is then calculated as:
\[
\frac{dc_{ex}}{dt} = \Pi - \eta 
\]

Before the increase in diffusion can be calculated, the influence of pipe diffusion needs to be calculated. First the number of atoms associated with pipes needs to be estimated, this is given as:

\[
g = \frac{2 \Omega pt}{b} 
\]

Pipe diffusion also has an activation energy, which is calculated as:

\[
\frac{Dp}{Db} = \exp \left( \frac{93.7e3}{8.314 \times T} \right) 
\]

Where Db is the lattice diffusion coefficient, set here to 0.0013. The factor by which diffusion is increased due to both vacancies and pipe diffusion can now be calculated, referred to here as Ddt;

\[
D_{dt} = 1 + \frac{C_{ex}}{C_{th}} + g \frac{D_p}{D_b} 
\]

This can then be added to the standard diffusion equation to calculate the actual diffusion rate:

\[
D_{total} = D_{dt} Db e^{-\frac{q}{kT}} 
\]
The model can be run to investigate altering any of the deformation parameters, and the different influences on diffusion can also be examined. As the model is programmed in MATLAB the model can be run and the data plotted very quickly.

6.1.2 Results

This model can be utilised to give a single value for diffusivity under given conditions, or can be used to give a diffusion enhancement curve based on altering one variable. For example, the diffusion rate (and the enhancement factor) can be calculated for a range of strain rates at a single temperature, or the effect of one strain rate at different temperatures can be calculated. This could simulate the effect of changing rolling speed, which is the most influential factor on strain rate, or the effect of cooling during rolling, which is known to be significant during commercial processing.

![Enhanced diffusion coefficient across rolling temperature range](image)

**Figure 127 Enhanced diffusion coefficient across rolling temperature range**

(Thermal in blue, enhanced in red)

Figure 127 shows how the predicted diffusion coefficient is enhanced by deformation, the enhancement to diffusion is larger at lower temperatures, but
is significant for the entire temperature range of interest. Figure 128 shows how the enhancement factor changes with temperature for strain rates of 1 and 10 s\(^{-1}\) and the relative contribution from pipe diffusion and vacancies.

![Graph showing diffusion enhancement for rolling temperatures, contributions from pipe and vacancy assisted diffusion](image)

This clearly shows how vacancy assisted diffusion is the major contribution to the enhancement of diffusion. The figure also shows that the enhancement is predicted to be reduced for higher deformation temperatures.

Figure 129 shows how the contributions from pipe diffusion and vacancies change with strain rate at a fixed temperature, again this shows the majority of enhancement comes from vacancy diffusion.
The model shows that while pipe diffusion would have some effect on diffusivity, the effect of the enhanced vacancy contribution would be far more influential on the overall diffusion coefficient at strain rates above $1 \text{s}^{-1}$. The role of vacancy diffusion is slightly diminished at higher temperatures, but is still orders of magnitude larger than pipe diffusion.

The results of this modelling were used to plan the deformation testing performed as part of the work. It was already decided that any deformation experiments would be first performed isothermally at the end of heat treatment temperature, thereby avoiding any thermal driving force for the growth of particles, allowing any change in particle size to be attributed to deformation effects alone.

It was observed that while diffusion could be significantly enhanced by high strain rate deformation, in order to observe a significant difference in a diffusion controlled process it would be necessary to deform at strain rates larger than 1, and for significant times (>1min). As the effects were confined almost exclusively to the deformation period, due to the rapid drop in vacancy concentration at the end of deformation, the time for enhanced diffusion could
be treated as the time of deformation. While the overall time for diffusion effects would be the time at temperature. Because of this, it would be necessary to heat the specimens rapidly, and quench immediately after testing, to make the enhanced diffusion time period dominant.

The modelling suggested that strain rates larger than 10 would be needed in order to achieve a twofold increase in the diffusion rate at 500°C. This led to the decision to use the ASP as a testing method as described in chapter 4.
6.2 KWN model

The next stage of modelling work was to adapt a model previously used to simulate the precipitation of dispersoids in a 7XXX series alloy to model the situation being examined in the work. This required several stages, as the model adapted had previously only modelled isothermal nucleation of precipitates, with no account for deformation effects on either diffusion or nucleation of particles.

As discussed in chapter 3 the Kampmann and Wagner model (KWN) calculates particle nucleation and growth over timesteps, allocating particles to “bins” based on size and calculating the changes that occur over time. The model is based on constitutive equations simulating the processes occurring, and these are calculated for each time step, allowing for a continuous development of the particle populations until the end of the time period. In this version the size of the time step is controlled by an adaptive function in order to minimise computing time (Robson & Prangnell 2001). The model consists of a series of Matlab functions referenced from two functions, an “initial” setup, which sets up the size bins and calculates some parameters, and a full “kinetics” function which repeats a loop of calculations until the full time is reached. This loop calculates:

1. Nucleation: Calculated from classical nucleation theory. The model calculates the critical radius size based on the Gibbs-Thompson equation.
2. Growth: Calculated from diffusion theory, and assuming a spherical shape for growth, from the experimental evidence this is clearly incorrect for dispersoids produced during heat treatments, however adapting the model would be complex and is unnecessary for modelling deformation effects on diffusion, it was therefore considered outside the scope of the work.
3. Change in matrix solute level: calculated from the initial concentration given as an input, and a mean field approximation based on the concentration from previous steps.

6.2.1 Model Function

The nucleation rate is modelled by first calculating the critical radius for nucleation $r^*$ using the equation:

$$ r^* = \frac{2\sigma V_a}{kT \frac{c_t}{c_\infty}} $$

Equation 45

Where $\sigma$ is the surface energy in Jm$^{-2}$, in light of a lack of an experimentally obtained value this was used to calibrate the model as described later. $V_a$ is the atomic volume, $c_t$ the concentration of manganese in the matrix, also an input, and $c_\infty$ the concentration of manganese in equilibrium with a planar interface of the dispersoid phase, calculated from Jmat pro.

This allows the energy of nucleation to be calculated as:

$$ G^* = \frac{4}{3} \pi r^2 \sigma $$

The rate of nucleation is then calculated as:

$$ J = N_0 \frac{kT}{h} e^{\left(\frac{-G^* + Q}{kT}\right)} $$

Where $Q$ is the activation energy of diffusion of manganese, as in the Militzer model. $k$ and $h$ are the Boltzmann and plank constants respectively. $N_0$ is the number density of nucleation sites, originally set to be the number density of solute atoms, however this was later adapted. Nucleated particles are then assigned to a size “bin” set up as part of the initial function.
Growth is calculated using the assumption of spherical particles. The growth rate is given as:

\[
\frac{dr}{dt} = \frac{D}{r} \left( c - c_r^a \right)
\]

Where \( D \) is the diffusion coefficient, calculated as would be expected at first utilizing experimental calculation of the diffusion coefficients (Hood & Schultz 1971), but in later work modified to include the predictions of the Militzer model, \( r \) is the radius of the particle, \( c^a \) is the concentration of manganese in the dispersoid phase, again taken from the Jmat pro prediction, although the literature suggests that this can vary during heat treatment. The concentration of manganese in the matrix at the interface, \( c_r^p \) is calculated using the Gibbs-Thompson equation:

\[
c_r^a = c_\infty^a \exp \left( \frac{2\sigma V_a}{kT} \frac{1}{r} \right)
\]

Where \( c_\infty^a \) is the mean field concentration of manganese. A continuity equation records the change in the precipitates in each timestep. Particles are assigned and re-assigned to bins during each timestep. Particles larger than \( r^* \) will grow, while particles smaller than \( r^* \) will shrink.

The model then calculates the mean field concentration of solute remaining by subtracting the particle concentration multiplied by the volume fraction of particles from the original matrix concentration.
The model operates in a loop, repeating the calculations, including assessing the next necessary timestep, until the end of the time set into the initial function is reached.

While the structure of the previous model was appropriate to predict the $\alpha$-Al-(Fe-Mn)-Si phase in this alloy, and has now been used to do so by other researchers (Du et al. 2013), all of the material specific constants had to be changed. The model was then recalibrated to fit with the first experimental results from heat treatments, and to account for the vagaries in determining values. This resulted in a model which could make predictions based on isothermal conditions, but not on realistic (non-isothermal) heat treatments for processing. The effect of diffusion enhancement could be included by simply multiplying the diffusion coefficient calculated by the enhancement factor given by the Militzer based model, this assumes that the enhancement of diffusion will take place evenly between solute species.

6.2.2 Sensitivity and calibration of initial model
Microstructural models can be very sensitive to inputs, so some analysis was performed to investigate how changing input parameters and constants changed the results. This was then used to calibrate the model towards the results of the heat treatments. The primary parameter in terms of running the model is the number of bins per decade; this controls the size resolution of model, and thus the speed of running the model. As the results of the model are plotted as a histogram (as with the results of the experiments) this also influences the number density of the particles within each bin, along with the smoothness of the curve.
Figure 130 Effect of changing bin sizes on predicted particle population (isothermal tests)

Importantly it can be seen that the curve is not significantly shifted in terms of mean particle radius, so this will not change the important position of the peak.

For further runs of the model the number of bins per decade was usually 50, as this most closely matches with the size of the histogram bins used in the experimental work.

The first input to the model that influences the results is the supersaturation of manganese within solution, from initial calculations utilising Jmat Pro this was believed to be around 0.85% after casting.
Running the model for several values of manganese supersaturation showed that while it has an influence on the size of the number density peak the value for manganese concentration does not significantly shift the predicted size distribution of the particles. For future work the value of 0.85 was used as predicted by the Schiel solidification model.

Another parameter that had to be calibrated was the effective surface energy of the particles; this had to be set to a significantly lower value than that previously used in other models, to result in a particle population that is close to that found in other work, and in these experiments. This fits previously discussed this fits with the idea that these particles have low surface energy, resulting and a dispersion of fine particles. It is difficult to assign a “correct” value for this parameter due to the semi-coherent nature of the particles, and no experimental value is available in the literature, however model predictions show it needs to be smaller than 0.0001Jm$^{-2}$ in order to give particle size predictions in the area seen experimentally shown in Figure 132. This is value is also significantly lower than the value used in other work modelling similar
alloys, (Du et al. 2013), and may be due to the difference in diffusion coefficients used. The work by Du utilised diffusion coefficients significantly lower, giving a diffusion rate over an order of magnitude slower, reducing the rate of coarsening.

Figure 132 Isothermal particle predictions for different values of surface energy

The experimental results show that the peak dispersoid size is ~30nm in radius, so this result is still slightly high; however there is another input which has an effect on the predicted particle size which is discussed later.

This shows that for a high dislocation density the particle density will be very high, however the particles will be small, lower dislocation densities increase the most numerous particle size, but reduce the density.

Once suitable values for the control inputs were found, some predictions could be made with the model. An isothermal plot (temperature of 775°C) is shown in Figure 133 for times of 1-5 hours. The emergent coarsening behaviour is clear, with the distribution shifting to the right and the peak number density decreasing as time decreases.
The results of this calculation are similar to the experimental results seen by Li et al in their experimental work at 600°C, again the predicted dispersoid size is larger, as would be expedited with the equilibrium volume fraction of dispersoids being higher at the lower temperature. The predicted coarsening rate is faster, which would not be expected, possibly suggesting the calculated diffusion rate is higher than in reality.
6.2.2 Thermal variance modelling

The next step was to adapt the model to predict the influence of thermal processing on the development of the second phase. This was done by removing the temperature as an input, and creating a new function which gave the temperature as an output based on the time. This allowed a heat treatment program to be modelled as an equation, as it would be programmed into a furnace. However, the existing model used the temperature only in the initial function, as this calculated all the thermally dependant constants and coefficients. These therefore had to be moved into the main loop of the model, and calculated for each timestep. This significantly increased the length of time taken to run the model, due to the increase in steps to be computed. This modification allowed the model to make predictions based on the type and length of heat treatment, along with modelling the effect of any post heat treatment heating during processing.

Figure 135 shows the predictions made by this version of the model of the particle population during the heat treatment.

![Heat Treatment Dispersoid Predictions](Image)

**Figure 135** Predicted particle populations for various times during two step heat treatment
In the results of following a profile of a 12h rise to 600 followed by an instantaneous drop to 500 and hold for up to 4 hours are plotted. As was found experimentally in this work, no particles are present at the peak of the rise, then during the hold particles nucleate, grow and coarsen. After adjustment the peak particle radius is around 100nm this is within an order of magnitude to the experimental results which found the peak dispersoid radius frequency was around 30nm, the model again predicting somewhat larger particles. The shape of the curve is slightly different, most likely due to the more complex behaviour of the dispersoids in the actual material.

This model was then used to make predictions of what would happen if the temperature was dropped after the end of the heat treatment, for example if the material was deformed at a lower temperature as happens in industry. This calculation was first performed without including any effects of deformation.

The predictions shown in Figure 136 predict that if the material is held at a lower temperature for 0.5h after heat treatment, two processes occur. Firstly the existing particles are grown significantly as further solute is removed from of
solution seen as the shift of the peak to the right and upwards. Secondly, new nucleation of particles occurs, with more nucleation occurring with a larger temperature drop, resulting in a higher peak at smaller particle sizes for lower temperatures. This is unlike what was seen experimentally, and suggests that this version of the model predicts an over-abundance of nucleation sites in undeformed material.

6.2.3 Nucleation site modelling

The original model used a nucleation calculation based on the number of solute atoms available; this assumed that nucleation could occur on a certain fraction of the available atoms, but that nothing else was required. From the literature and experimental evidence it is clear that in this alloy nucleation occurs on dislocations, therefore it was decided to adapt the nucleation calculation. This new calculation used the dislocation density (in m\(^{-2}\)) to calculate the number of available nucleation sites, assuming that nucleation could occur at a point within a certain number of atoms of the dislocation line. This gave a nucleation site density equation of:

\[
nad = \frac{\rho N_d}{\lambda}
\]

Where \(nad\) is the nucleation site density, \(\rho\) the dislocation density, \(\lambda\) the atomic spacing and \(N_d\) the number of atoms (per unit length) that could act as nuclei.

This simulates the atoms in the strain field around the dislocation. This required the creation of a dislocation density function, which was taken from the Militzer based model described earlier. This then created a nucleation site function which was influenced by deformation.

These functions were then linked within the model so that temperature and strainrate profiles could be included into a model calculation, and a result
obtained. This model could then be used to make predictions about the particle population after heat treatment, after deformation, and after thermomechanical processing.

The predicted dislocation density variation with strainrate is given in Figure 137

![Figure 137 Dislocation density with strainrate at 775K](image)

Once the nucleation site density was linked to the dislocation density the static dislocation density becomes an input. Varying the input value dislocation density (representative of the dislocation density during heat treatment) has a significant effect on the outcome of a model, as this controls the density of nucleation sites. A plot for a surface energy value of 0.001 Jm\(^{-2}\) and number of atoms per unit length of 10 is given in Figure 138. This again predicts larger particles than are seen unless unrealistically high nucleation site densities are used, so the value of surface energy had to again be reduced to 0.0001 Jm\(^{-2}\).
The nucleation site density was one of the values used to calibrate the previous model used as a framework (Robson & Prangnell 2001). Including the new nucleation function allowed the model to be better calibrated towards experimental results, shifting the post heat treatment prediction closer to the 20-30µm peak particle size for further calculations. The number of atoms per unit was increased to 100, while the static dislocation density was set as $10^{10}$ m$^{-2}$. This produces a curve close to experimental results, with a slightly higher, narrower peak.
Figure 139 Post heat treatment particle distribution, model including nucleation on dislocations

6.2.4 Including deformation effects

The first stage of modelling the effect of deformation was to include enhanced nucleation sites on the model. This was done by running the model for the heat treatment profile, and then for 0.1h at 500°C with an enhanced nucleation site density, calculated from the function describe earlier. This is representative of a torsion test, but does not yet include enhancement of diffusion. Figure 140 shows the end of heat treatment curve, plus results for 0.1h at 500°C, with and without deformation.
Figure 140 Effect of 0.1h hold at 500°C with and without enhancement of nucleation sites

The difference between the red (enhanced nucleation) and blue (unenhanced) is very small, both show a small amount of coarsening, there is a slight kink on the right of the red curve, but the shape, height and position of the peak is not significantly different. This shows enhancing the nucleation site density in material held at the heat treatment temperature has virtually no effect, demonstrating that there should be no thermal supersaturation of manganese to precipitate out. This supports the theory that precipitation seen in the experimental results is due to a deformation induced mechanism, the original supersaturation should be removed.

Modelling the result of deformation and a drop in temperature shows how significant the effects of deformation processes on nucleation could be on the particle population of commercially produced material in terms of new particle nucleation. Figure 141 shows the prediction of the model for conditions similar to the lower temperature torsion tests.
Figure 141 Nucleation only model demonstrating effect of strain on dropped temperature particle evolution for 0.1h after heat treatment

Figure 141 contains several predictions; the black line is the post heat treatment curve. The blue and dark blue solid lines represent temperature drops for the same length of time of 480°C and 450°C respectively. The broken lines also include enhancement of the nucleation sites for a strainrate of 0.1s⁻¹.

Temperature drops without deformation are now seen to only produce growth on existing particles; this is closer to the experimental results, although the peak is narrower than that seen in experimental results (Figure 99).

Temperature drops combined with deformation enhanced nucleation density are shown to have a large effect, with a huge number of new particles forming (<10nm in radius) along with the growth of existing particles seen around 25-30nm in radius.

The final step in the development of the model was to incorporate the effect of diffusion enhancement into the model. The full diffusion model was not incorporated into the timestep function; instead a simplified relationship was
used, taking the enhancement factor from the Militzer model and incorporating it into the diffusivity calculation.

This final model allows full simulations of the predicted nucleation growth and coarsening of particles during thermomechanical processing, incorporating the effects of both thermal processes and deformation mechanisms. Figure 142 shows predictions after heat treatment plus an additional 0.1h, with either no deformation, or a strainrate of 1s\(^{-1}\) and 20s\(^{-1}\), this is representative of the isothermal torsion tests performed as part of this work.

As would be expected from theory, simply incorporating strain for 0.1h after the heat treatment results in a slight coarsening effect compared to unstrained material but there is no major change in the particle distribution. Notably this coarsening is not as large as that seen in the experimental results, shown in figure Figure 139. This suggests that the diffusion enhancement factor is not an over-estimate, and also consistent with the theory that the interfacial energy of the dispersoids is increased by deformation. The fit of the model to the experimental results could be further improved by incorporating a function.
which increased the interfacial energy for deformation; however this would require a better understanding of the interface, and the role of deformation on changing its properties.

![Particle size distributions with calculated densities. 500°C deformation experiments](image)

The lack of new nucleation does not match the observed change in particle populations seen in the experimental work, shown in Figure 143, demonstrating that there must be an addition process occurring during deformation that causes the change in particle distribution observed in experiments. This process must be creating a driving force for nucleation of new particles. As the origin of this driving force is unclear no attempt has been made to include this observation into the model. Constitutive models for calculating the effect of excess vacancy concentration on the segregation of alloying elements have been developed to model damage during irradiation, this type of calculation could be incorporated into the KWN model, but would add an extra level of complexity. Calibration of such a model would require a great deal of experimental work, most likely utilising TEM-EDX.
Figure 144 shows a simulation of the dropped temperature tests in comparison to the predictions made in Figure 141. The blue dotted lines representing material deformed at different strain rates.

![Graph showing model predictions of effect of strain, dropped temperature tests](image)

This predicts that material deformed at lower temperatures there is an even larger effect to the processes already seen in Figure 141, the growth of particles is enhanced further, while the newly nucleated particles are present in even higher numbers. This is due to the increased diffusion coefficient allowing the solute to reach particles faster. Note there is a trend towards higher numbers of small particles in the slower deformed material, and less growth of pre-existing particles, as the diffusion rate is slower. The predicted newly nucleated particles are very small.

These results agree in part with those of the experiment work (Samples 3A and 3B) in that the shape of the curve is a binomial distribution, with an extremely large peak around 10nm, representing newly nucleate particles, while the preexisting particles are slightly increased in size at around 30nm. In the experimental work it was found that the pre-existing particles were much
larger. This discrepancy is likely due to the very low surface energy term in the model allowing more nucleation of small particles rather than growth of pre-existing particles. While this value was produced good results for heat treatments, as discussed previously there is substantial evidence for a change in the nature of the dispersoid-matrix interface, and for deformation it is likely that the constant value used here is too small, and that a more accurate value for affected particles would reduce the number density of the newly nucleated particles peak, and increase the peak radius of the pre-existing particles. This would also likely result in a larger spread to the distribution.

While not matching the results of the experiments exactly, the modelling results add further weight to the points made in the discussion. The enhanced coarsening seen in Figure 142 is similar to that observed in the isothermal tests, although is actually smaller than the observed change. As the model appears to overpredict thermal coarsening, this also adds evidence to the theory that the interface of the particles is altered, enhancing spheroidization and coarsening further. The model does not predict new nucleation of particles during isothermal deformation, but over predicts nucleation during deformation at lower temperatures. This result also suggests that the interfacial energy is not constant during deformation, and that there is a larger driving force for growth on pre-existing particles.

The model could be improved by acquiring better values for the thermodynamic data through us of techniques such as DSC, as has been done previously for other models utilising the KWN structure, (Kamp et al. 2006). An experimentally or ab-initio calculated value for the interfacial energy may also help calibrate the model for thermal processes, but further work would be needed in order to understand the interface during deformation.
Chapter 7 - Conclusions

This chapter draws together the main conclusions of the work performed, and highlights areas of interest and possibilities for future investigation.

7.1 Conclusions

This work has shown how high strain rate, high temperature deformation alters the particle populations of a dispersoid containing, model 3XXX series alloy. Experimental results have shown that there are several interacting processes occurring during deformation, and that these are not simply normal thermal mechanisms, or a simple rate increase in particle evolution.

It has been demonstrated that the dispersoid particles change in shape under high strain rate deformation, losing the straight edges and sharp corners of the post heat treatment particles, and becoming more rounded. This has been demonstrated using SEM, image analysis derived particle statistics, and by TEM observation of particles. This shape change has been attributed to the breakdown of coherency at the particle-matrix interface, resulting in an increase in surface energy creating a stronger driving force for spheroidization.

It has also been demonstrated that there is an enhancement to coarsening by deformation during isothermal deformation, likely to be due to the increase in diffusion rates. This matches with the results of modelling which show a prediction of a small increase in peak particle radius for isothermally deformed material.

The final finding has been the observation of new nucleation of dispersoid particles, along with a corresponding increase in volume fraction of the dispersoid phase, in material deformed isothermally at the same temperature as
a prolonged prior heat treatment. This was not expected as examination of the heat treatments performed showed that all supersaturation of manganese should have been removed, and modelling of the system also suggested that there should be no new nucleation of particles without a drop in temperature. This process has not been fully explained, but several possibilities have been proposed, with the actual mechanism likely involving interaction between solute manganese and dislocations or other deformation induced defects, potentially increasing the local level of manganese around nucleation sites, such as dislocation clusters.

Experiments performed at lower temperatures showed that deformation at a temperature lower than the end of heat treatment temperature resulted in a different evolution route for the dispersoid population. In undeformed material, a drop in temperature led to the growth of existing particles, with little or no new nucleation. Deformation allowed nucleation to occur, creating a much higher number of particles and allowing a larger volume fraction of $\alpha$-Al-(Fe-Mn)-Si phase to form. This is most likely due to the increase in dislocations due to deformation providing many more possible nucleation sites, giving the solute shorter distance to diffuse, combined with the rapid diffusion and segregation effects seen previously.

These results suggest that in industrial processing, where the temperature continually decreases while the material is rolled from billet to thin strip, particle nucleation and growth will be concurrent processes. Rather than the particle population growing and coarsening over time, new particles will be continually formed on dislocations. Additionally the particles will be more rounded than those found in heat treated material, and have higher surface energies than would be expected.
The higher volume fraction and smaller particle size will combine to make the particles have a considerably stronger Zener pinning pressure, resulting in an increase resistance to recrystallization and a higher retention of the rolled texture, rather than the recrystallized cube texture.

### 7.2 Further work

Drawing from the conclusions there are still areas of interest which could be investigated following this work. The nature of the dispersoid particle interface after deformation could have a significant effect on the role of the particles in controlling the properties of industrially processed materials. As such, characterising these interfaces after deformation should provide useful information that could be incorporated into a model for particles development, similar to the KWN model described in chapter 7. Techniques similar to those used in previous work on dispersoid interfaces could be used on deformed material. TEM analysis of the interface along with TEM EDX of the particles to investigate if there is a compositional or structural difference would provide most of this information. This would have to be done on a relatively large number of particles so that some statistical data could be acquired and the nature of the boundaries properly understood. Measurement or calculation of the actual energy associated with the dispersoid matrix interface would be more complex, probably requiring ab-initio modelling or similar.

To investigate the segregation mechanisms similar techniques, such as TEM-EDX profiles from a small, new nucleated, dispersoid could be used. Alternatively techniques such as atom probe tomography could be used to map the concentration of elements around a feature, such as a dislocation cluster, in deformed material. If the mechanisms of solute segregation can be properly understood, it would be possible to incorporate a function into the existing model framework and create an accurate model for particle development during thermo-mechanical processing.
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