Study of concurrent recovery and precipitation on the mechanical behaviour of Al-Mg alloys with small additions of Cu

by

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Abstract

Aluminum-magnesium alloys are commonly used as wrought products in the automotive industry. Cold forming of such alloys leads to strengthening by work hardening but some of this strength can be lost by exposure to elevated temperatures leading to recovery. Such softening by recovery occurs when car body panels are subjected to the industrial paint bake cycle (160-200°C for ≈ 30 min).

It has been previously shown that small (<< 1 wt%) additions of Cu to Al-Mg alloys can suppress softening under simulated paint bake conditions owing to the formation of small solute clusters. Two mechanism(s) could control this phenomenon; precipitation hardening and precipitation induced suppression of recovery. Through this thesis, it was shown that precipitation hardening due to solute clusters / GBP zones is the dominant effect, it being significant enough to counterbalance strength loss due to recovery. Using a combination of techniques, with a particular emphasis on atom probe tomography, the precipitation hardening in solution treated (undeformed) samples could be quantitatively related to clusters / GBP zones. A quantitative evaluation of the effect of pre-deformation on the formation of clusters / GPB zones was also obtained showing that dislocations negatively affect the strengthening owing to the effect of rapid vacancy loss to dislocations. This conclusion was reached thanks to a technique developed as part of this thesis that allows one to quantitatively assess, separately, the effects of precipitation hardening and forest hardening from a detailed analysis of the work hardening response upon yielding.
Lay Summary

The transport industry contributes significantly to the production of CO₂ which, by itself, accounts for the largest proportion of green house gases accumulating in the atmosphere. Using aluminum alloys to reduce the total weight of vehicles on the road and consequently the total emission of CO₂ can potentially reduce the impact of this industry on the environment. To extend and optimize the use of aluminum alloys in automotive applications, namely inner body panels, a better understanding of the concurrent effect of hardening by precipitation and softening by recovery during manufacture has to be attained. In this work, this has been accomplished by means of experimental characterization and modelling, using similar conditions as used during the manufacture of car body panels. Among other findings, a relationship between characterized precipitates and the mechanical strength of the studied alloys was established. Furthermore, it was seen that deformation negatively affects the strengthening by precipitation.
Preface

The work done in this thesis has been developed by the author in continuous collaboration with his Ph.D. supervisor, Prof. C. W. Sinclair. All experiments done at UBC have been conducted by the author; these include solution and aging heat treatments, uniaxial tensile testing and electrical resistivity (Chapter 5 and 6).

The alloys used in this work were provided by the Novelis Global Technology Centre. Colleagues at Novelis also providing input for the experimental design in the early stages of this thesis and aided with providing facilities for the characterization of samples. The observations made by STEM in SEM in Chapter 6 were performed on material processed at UBC by the author, while the final preparation and microscopy observations were made at Novelis Global Technology Centre, Kennesaw GA. The author performed this analysis himself at Novelis during a 5-day visit in July 2015, with assistance from the Novelis technical personnel.

In Chapter 5 and 6, the Atom Probe Tomography (APT) results were the product of a collaboration with Dr. B. Gault and H. Zhao, from the Max-Planck-Institut für Eisenforschung, Düsseldorf. The experimental conditions for the material analyzed by APT were selected by the author. These selected thermo-mechanical treatments and preliminary sample preparation for APT were performed at UBC before shipment to MPIE. The final preparation stage, APT observations, and volume reconstruction analysis was done by H. Zhao and Dr. B. Gault. The author was involved in all stages of the interpretation of the final results. The Pair Correlation Analysis shown in Chapter 5, applied to the analysis of clusters from APT data, was developed in collaboration with Dr. F. De Geuser from University Grenoble Alpes, CNRS, Grenoble INP, SIMAP. The DSC studies, shown in Chapter 5 and 6, were carried out by the author during a three-week stay at the University Grenoble Alpes, CNRS, Grenoble INP, SIMAP, in 2015.

Finally, a journal paper based on sections of Chapter 5 has been accepted for publication in Acta Materialia: S. Medrano, H. Zhao, F. De Geuser, B. Gault, L. T. Stephenson, A. Deschamps, D. Ponge, D. Raabe, C. W. Sinclair, ”Cluster hardening in Al-3Mg triggered by small Cu additions” Available online on August 30th, 2018. https://doi.org/10.1016/j.actamat.2018.08.050
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Chapter 1

Introduction

The negative environmental consequences of greenhouse gases (GHG) has led multiple industries to develop technologies to reduce their emissions. The global transportation industry (e.g. automotive, aerospace, marine) is the second largest source of GHG emitters, accounting for approximately 24% of the total emission of CO$_2$ in the atmosphere [1]. In particular, road transportation accounts for 75% of the total share of emissions for this sector, leading the increase in emissions within it (a total increase of 68% from 1990 to the latest IEA evaluation in 2015) [1]. One strategy to reduce the volume of GHG produced by the transportation sector is by vehicle weight reduction. In the case of automobiles, reducing the weight by 10% results in a 7% reduction of the amount of fuel required to travel the same distance [2]. Weight reduction has been achieved through a combination of design and material substitution, particularly replacing steel components with lower density metals such as aluminum and magnesium [3]. Aluminum has progressively increased its share among the materials being used in automobiles, with a projected increase of 13% from 2015 to 2020. An area of particular increase will be for its use in car body panels, where it is projected that it will have an increase of 83% by 2020 [4].

Automotive body panels are divided into inner and outer panels, both having different requirements. Outer panels have to retain a yield strength of at least 200 MPa after so-called paint bake (a heat treatment between 160 to 200 $^\circ$C, from 20 to 45 minutes), have flat hemming capability, good surface appearance, and be corrosion resistant [5]. Inner panels require the ability to be formed, be weldable and capable of retaining a high yield strength after paint bake [5]. The most common aluminum alloy used for inner panels belongs to the 5XXX series, which have a comparatively low cost and high formability, making them attractive for this application [5]. The confinement of 5XXX series to inner panels is due to the formation of visually unattractive surface marks, developed when these alloys are subjected to deformation during forming.

The alloys used as inner panels attain their high strength due to deformation (work hardening). Some portion of this strength is however lost during subsequent heat treatments required in the ‘paint bake’ cycle. This is inefficient as the lost strength has to be accommodated by the use of thicker part sections or more complex design.

Alloying that leads to precipitation can be used to partially counteract the softening experienced in the
Figure 1.1: Aging behavior of Al-3.35at.%Mg-0.25 at.%Cu (Al-3wt.%Mg-0.6 wt.%Cu) alloy and AA5754 system (Al-3.35at.%Mg) at 180 °C, following a pre-strain of 10%. These are conditions similar to those experienced in a paint bake cycle [6].

‘paint bake’ heat treatment. The addition of Cu, for example, to 5XXX (Al-Mg) alloys is known to be effective in producing precipitation hardenable alloys. The relatively ‘large’ additions of Cu in conventional Al-Cu-Mg alloys (2xxx series alloys) is, however, undesirable as it raises alloy cost and reduces weldability due to hot cracking sensitivity [7].

It has been shown that even small additions of Cu to 5XXX series alloys can still be beneficial to strength retention (or even improvement) during the paint bake process (Figure 1.1). Few studies of origins of these improved properties exist in the literature. While it is understood that it is precipitation that is at the root of these improvements, the relation between this precipitation and strength is not understood [8]. In a broader context, the effect of pre-deformation on precipitation, the relationship between precipitation and static recovery, and their combined contribution to the mechanical strength evolution are still subjects of study [9]. This thesis seeks to address these issues, with a specific aim of improving the post paint bake strength of 5xxx alloys with small additions of Cu, by improving our understanding of the coupled microstructural phenomena that occur during processing.
Chapter 2

Literature Review

The following chapter provides an overview of the current understanding of the microstructural and mechanical property changes that occur during the low temperature ($T < 250^\circ\text{C}$) heat treatment of aluminum alloys. This chapter starts by illustrating basic principles through two classic binary aluminum alloys, Al-Cu and Al-Mg alloys. The Al-Cu alloys section will be used to introduce the general concepts involved in precipitation strengthening, whereas the section on Al-Mg alloys will discuss concepts related to the softening of wrought alloys by ‘recovery’. These are the two fundamental processes controlling the evolution of the mechanical strength of the Al-Mg-Cu alloys studied in this thesis. Following this, a review of clustering and cluster/precipitation strengthening in Al-Cu-Mg and Al-Mg-Cu alloys will be presented. Finally, our current understanding of the coupled effects of precipitation and recovery will be discussed.

2.1 Age Hardening of Binary Al-Cu Alloys

The first systematic studies of precipitation hardening in aluminum alloys were performed in the Al-Cu system [10]. Like many other age hardenable aluminum alloys, the Al-Cu system does not proceed from supersaturated solid solution directly to an equilibrium precipitate phase. Instead, it undergoes a complex transition through a series of metastable phases before reaching the equilibrium precipitate phase. The low-temperature precipitation sequence in age-hardenable Al-Cu alloys progresses from the supersaturated solid solution ($\alpha_{ss}$) via [11–13]:

$$\alpha_{ss} \Rightarrow \text{GP zones} \Rightarrow \theta'' \Rightarrow \theta' \Rightarrow \theta$$

The exact sequence of phases observed depends on the aging temperature and alloy composition as each of the phases noted above has its own solvus curve (Figure 2.1). Thus, the progression shown above is only observed when the aging temperature is low enough that the GP zone solvus is crossed. The preference for the sequential formation of these metastable phases at low temperature has been attributed to an easier nucleation pathway associated with lower activation barriers between each of the metastable phases compared to the barrier separating the solid solution from the equilibrium phase.

The activation energy between the metastable phases is presumed to be lower because the crystal struc-
Figure 2.1: Al-rich corner of the Al-Cu phase diagram indicating regions of stability of the different transition phases observed during precipitation in this system.

[9].

Tures of the intermediate phases are more similar to one another than that of the equilibrium phase and the solid solution, meaning that better lattice matching between the metastable phases exists and, consequently, lower interfacial energy [9]. For very small nuclei, the interfacial energy is a dominant term (due to the Gibbs-Thompson effect) in the classical description of the nucleation barrier [14].

Generally speaking, the first metastable product arising from the decomposition of the supersaturated solid solution at low temperature is known as Guinier-Preston zones (GP or, in older literature, GP-I zones). GP zones in Al-Cu alloys were first detected by X-ray diffraction (XRD) [15], and changes in electrical resistivity [16], then later by Transmission Electron Microscopy (TEM) [9, 17]. In Al-Cu alloys, the GP zones are observed as fully coherent single, or multi-atomic-layer thick Cu discs or plates, lying in the 100-Al planes [11] (Figure 2.2(A)). The particular shape of the GP zones in Al-Cu alloys arises from the large atomic volume difference of Al and Cu, the plate shaped morphology minimizing the elastic strain energy [9, 18].

The \( \theta'' \) phase (sometimes denoted as GP-II), comprises two parallel layers of Cu atoms laying on the Al \{001\} planes, separated by three parallel planes of Al atoms resulting in the \( Al_3Cu \) stoichiometry (Figure 2.2(C)). This phase is often found to form heterogeneously on pre-existing GP-zones [19].

Unlike GP-zones and \( \theta'' \), which are both fully coherent, the body-centered tetragonal \( \theta' \) phase forms as broad plates, the faces of the plates being coherent with the \{100\} planes of the aluminum but incoherent...
on the edges of the plates [11]. Nucleation of this phase is found to be difficult, resulting in it precipitating heterogeneously on grain boundaries and on dislocations [11, 12]. The $\theta'$ phase is richer in Cu than $\theta''$, having a stoichiometry of $Al_2Cu$. Finally, the stable $\theta$ phase shares the same body centered tetragonal crystal structure and $Al_2Cu$ composition, but is fully incoherent with the matrix. It is often found to precipitate heterogeneously on pre-existing $\theta'$ particles.

Figure 2.6 shows the evolution of hardness with aging time for the case of an Al-4wt.%Cu alloy aged at 130 and 190°C. The mechanistic origins of this evolution are typically described following the approach illustrated in Figure 2.3. In the earliest stages of aging, the formation of GP-zones occurs, removing Cu from solid solution this leading to a drop in yield strength. This in turn is compensated by the formation of the GP-zones whose strength increases as aging proceeds. The critical shear stress for a dislocation to move through a population of small and, therefore, weak GP-zones/precipitates can be described via the Friedel model as [20]:

$$\tau_c = \frac{2\Gamma \beta^2/3}{bL_s}$$

(2.1)

where $\Gamma$ is the dislocation line tension ($\approx 0.5Gb^2$), $b$ the magnitude of the Burgers vector. The mean square spacing of precipitates, $L_s$, is calculated directly from the number of particles per unit area on the glide plane, $L_s = (N/a)^{1/2}$. The magnitude of $L_s$ is expected to decrease in the early stages of aging due to the
increasing number density of particles formed by nucleation, this giving an important contribution to the increasing strength at early times. The strength of an individual GP-zone/precipitate is described by the parameter $\beta_c = \cos \psi_c$ (Fig. 2.4). Here, $\psi_c$ is the critical angle that a dislocation bends before overcoming the GP-zone/precipitate (Figure 2.4). In the Friedel limit the critical angle is large ($120^\circ \leq \psi_c \leq 180^\circ$) meaning that the dislocation bends only a small amount before overcoming the obstacle. In this limit, the dislocation typically overcomes the GP-zone by shearing or cutting through it [21] (Figure 2.5a). While the detailed process of a dislocation cutting through a GP-zone/precipitate is complex, it has been found that a linear evolution of $\beta_c$, this proportional to the mean precipitate size (i.e. $\beta_c \propto \bar{r}$), generally reproduces experimental results in an acceptable manner [22]. Thus the initial increase in strength in Figure 2.3 is due to the strengthening of GP-zones, due to their increase in size, combined with a higher number density of particles (decreasing $L_s$) during aging.

![Figure 2.3: Calculated contributions to the yield stress during aging in Al-4wt.%Cu alloy, aged at 150 °C.](image)

The above process occurs through the formation of $\theta''$ particles, progressively evolving towards the formation of the $\theta'$ phase. At the point when the $\theta'$ phase is the dominant phase in the microstructure, the particles have become sufficiently strong that cutting is no longer the interaction mechanism between dislocations and precipitates, and rather the dislocation bypasses the precipitate by bowing around it (dislocation or Orowan looping [20], Figure 2.5b). When looping becomes dominant, $\beta_c$ is considered to reach a constant value equal to 1. Also, as the microstructure changes from a fine, high number density of GP-zones/$\theta''$ precipitates to coarser $\theta'/\theta$ precipitates, the number density must decrease. In this case, $L_s$ increases and, at
constant $\beta_c$, the yield strength is predicted to drop.

**Figure 2.4:** Interaction between precipitate and moving dislocation. [20]

Implicit in equation 2.1 is that $L_s$ and $\beta_c$ are related to one another. For precipitates that are stronger than the Friedel limit ($\psi_c < 120^\circ$) the relationship between precipitate strength, size and number density needs to be evaluated numerically. Classically, this has been done using aerial glide simulations as previously reported in [20, 25, 26]. Additionally, this expression assumes point obstacles as depicted in 2.4, not accounting the effect of precipitate’s geometry on, for example, the effective distance between obstacles [20, 27], further constraining the effectiveness of this expression for early stages of precipitation.

Finally, it is worth noting that minor additions of other alloying elements can have a major effect on the precipitation sequence in Al-Cu alloys [18, 28]. It was realized early, for example, that small additions of Sn, Cd, and In could help catalyze the nucleation of the $\theta'$ phase largely, if not entirely, avoiding the formation of GP-zones and $\theta''$ precipitates [18, 28, 29], having a finer dispersion, resulting in a higher strength (Fig. 2.6). The study of the source of the remarkably different aging process due to additions of micro-alloying elements, have been supported by the development of Atom Probe Tomography (APT) [11, 18, 30]. This is a technique capable to study materials with atomic resolution, allowing study of very early stages of precipitation, as well as the distribution of the previously mentioned small addition of alloying

**Figure 2.5:** a) Particle shearing, b) Orowan looping [18, 24]
elements. The use of APT on Al-Cu systems have revealed features that precede the formation of GP zones, denominated clusters [18], as well as clarification of the role of the mentioned micro-alloying elements [11] during aging. Due to the substantial effect on the study of early stages of precipitation in Al alloys, a detailed description of this experimental technique will be provided later in this literature review.

Figure 2.6: Hardness evolution of Al-2.5 wt.% Cu alloy aged at 200 °C.

[18]

2.2 Softening by Recovery in Wrought Binary Al-Mg Alloys

Unlike the Al-Cu alloys discussed in the previous section, commercial alloys based on the Al-Mg system are not precipitation hardenable, within the industrially relevant times and temperatures. Instead, Al-Mg alloys are referred as wrought alloys, their strength coming from solid solution, and work hardening. By adding Mg to pure Al, the material can be strengthened substantially due to plastic deformation (so-called work hardening), compared to pure Al, which work hardens much less. The source of this effect has been associated to dislocation drag and pinning by Mg in solid solution, inhibiting dynamic recovery (loss of dislocations taking place during plastic deformation) [31–33]. The challenge outlined in the introduction to the thesis is that annealing of a wrought alloy (e.g. paint bake process) will lead to a reduction of the stored dislocation density and, therefore, strength. This softening due to annealing, following work hardening, is known as static recovery [32]. At a macroscopic level, the main manifestation of recovery is the gradual reduction in the hardness/yield strength during time after deformation, the rate of softening being faster at higher temperature (Figure 2.7).

For sufficiently high temperatures and, in a lesser degree, higher prior imposed deformation, recovery will give way to the process of recrystallization, e.g. Go et al. [34] observed onset of recrystallization after annealing > 10^4 s at 275 °C, for material deformed an equivalent strain of ε =0.58 (see Figure 2.8). By increasing the annealing temperature by a ΔT =25 °C, the time required for the onset of recrystallization was reduced by approximately an order of magnitude per increment of annealing temperature. While recovery is characterized by a steady drop in yield strength (linear in a logarithmic time-scale, Fig. 2.7), recrystallization is characterized by a rapid drop in strength (sigmoidal in a logarithmic time-scale, Figure 2.8) [35]. Here,
the focus will remain on recovery owing to its importance during the processing conditions experienced in the paint bake cycle of automotive parts. The reader interested in more details about recrystallization in Al-Mg alloys is pointed to the review in [33].

![Graph](image1.png)

**Figure 2.7:** Yield stress evolution during annealing of an Al-3 wt.% Mg alloy, cold rolled (equivalent strain $\varepsilon=3$). The annealed temperatures are shown in the graph [32]

![Graph](image2.png)

**Figure 2.8:** Yield stress evolution during annealing of a AA5754 alloy, cold rolled (equivalent strain $\varepsilon=0.58$). The annealed temperatures are shown in the graph [34]

At the microstructure level, recovery is characterized by the rearrangement of dislocations leading to a reduction of the dislocation density relative to the as-deformed state [32]. From a process point of view, first, at low levels of plastic deformation (10% strain), the material’s microstructure will be populated by individual arrangements of dislocations (Figure 2.9 (a)). Larger levels of deformation will result in the formation of cells, these being volumes of the material delimited by densely populated arrangements of dislocations (cell walls, Figure 2.9 (b)). Upon annealing, the dislocations forming the previously described cell walls will consolidate (Figure 2.9 (c)), resulting in a sharper boundary and evolving into the so-called
subgrains, these separated by well-defined low angle sub-grain boundaries (Figure 2.9 (d)). These sub-grains will continue growing with further annealing (Figure 2.9 (e)). The sub-grains developed on recovery will contain a low density of dislocations compared to the delimiting walls [33].

![Figure 2.9: Recovery evolution in a deformed material](image)

The rearrangement of dislocations during static recovery is governed by the processes of dislocation climb and cross slip [32]. An important parameter in determining the rate of these processes is the material’s stacking fault energy (SFE). Material with a high SFE, like aluminum (SFE ≈ 170 mJ/m²), show higher rates of both dislocation climb and cross slip and, thus, high rates of recovery compared to low stacking fault energy materials [35]. The presence of Mg as a solid solution element in Al has two opposite effects on recovery. On the one hand, Mg in solution leads (for the same level of strain) to a reduction in dynamic recovery, allowing for a higher density of stored dislocations and, consequently, a higher work hardening rate. On the other hand, this higher dislocation density is translated to a higher driving force for static recovery compared to pure Al, at the same level of deformation, resulting in faster static recovery process in Al-Mg alloys (compared to pure Al) [32, 33].

Several models have been developed to predict the reduction in yield stress due to recovery [35]. Nes [32] proposed a detailed model for static recovery, accounting for the cell/subgrain structure, and the dis-
location density within subgrains. While the Nes model was shown to well predict the softening due to recovery in Al alloys [32, 36], it requires calibration of a large number of fitting parameters that can be difficult to experimentally assess [34].

Following shortly after the Nes model was proposed, a second similar model was proposed by Verdier et al. [37]. While the basic physical principle of the Nes and Verdier models are the same, the Verdier model has an advantage in that it requires fewer parameters to be assessed. The Verdier model starts from the same assumption as the earliest models for recovery have relied [37], namely, that the rate of reduction in the flow stress ($\sigma$) is proportional the plastic strain rate ($\dot{\varepsilon}_p$), accomplished by dislocations as they move during recovery;

$$\frac{d\sigma}{dt} = \sigma = -E\dot{\varepsilon}_p \quad (2.2)$$

with $E$ being the Young’s modulus. Using the Orowan equation [37] to relate the plastic strain rate to the dislocation density, and assuming thermally activated dislocation motion, then one obtains,

$$\sigma_{\text{Verdier}} = \frac{-64\sigma^2\nu_D}{9M^2\alpha^2E} \exp\left(-\frac{U_0}{kT}\right)\sinh\left(\frac{\sigma V}{kT}\right) \quad (2.3)$$

Where $\sigma$ is the dislocation contribution to the yield stress, $\nu_D$ the Debye frequency, $M$ the Taylor factor, and $T$ the temperature. Typically the activation energy $U_0$, and the activation volume $V$ for recovery are taken as adjustable parameters. While the expected values for the activation energy would be ones (in a simple approximation) associated to the activation energy for the mechanisms envisioned for recovery (e.g. diffusion assisted dislocation climb and/or cross slip), reported values for an Al-2.5 wt.% Mg alloy [37] and AA5754 [34] are significantly higher[37]. Similarly, the activation volume should also be consistent with the expected mechanism, but has been reported to be a decreasing function of the pre-strain [34, 37]. This observation has been argued to be evidence of recovery within cell walls/ subgrain boundaries as being the dominant effect [32].

Precipitation is possible in Al-Mg systems, but requires aging times that are outside of the industrial interest. Furthermore, for parts constituted by this alloys and subjected to temperatures in the range from 50 °C to 200 °C during operation, the observed intergranular precipitation results in entitlement and corrosion problems [38]. During aging at temperatures below 100 °C, the generally accepted precipitation sequence is [13, 38–40]:

$$\alpha_{ss} \Rightarrow GP \Rightarrow \beta'' \Rightarrow \beta' \Rightarrow \beta$$

Where the use of the term GP zone is used, as discussed in the previous section, in the sense of being the first feature associated to precipitation. Its presence has been detected by means of increase of resistivity during aging [41], DSC (as a the first exothermic peak in naturally aged samples) [13, 39], and a modulated periodicity along the $<100>$ direction in HRTEM studies [13]. Using SANS, Roth and Raynal [42] proposed the GP zones to have a sphere-like shape, with a radius between 2 to 6 nm, and a concentration
Figure 2.10: a) Hardness evolution for Al-10wt.%Mg and Al-5wt.%Mg during aging at 30 °C. b) Resistivity evolution of Al-10wt.%Mg system aged at the indicated temperatures from 20 to 25 at.% of Mg. These finding have been further supported by Yi et al. [43] in their APT observations of a AA 5083 alloy, aged at 50 °C for 24 months. The β′′ phase (sometimes identified as well as GP zones [13, 40], or ordered GP zones), posses a L12 crystal structure with a Al3Mg stoichiometry [13, 39, 43], the β′ phase posses a HCP crystal structure with a Al3Mg2 stoichiometry, and the the stable β phase has a FCC structure with a Al3Mg2 composition [39, 43]. Sato et al. [40] investigated the hardness and resistivity evolution in a Al-5 wt.%Mg and Al-10 wt.%Mg aged between -30 to 100 °C, revealing that no hardening effect can be observed after more than 3000 hrs at room temperature in the Al-5 wt.%Mg, while the Al-10 wt.%Mg system barely increases in the same period span (Fig.2.10a. In contrast, and as mentioned in the description of the GP zones for this system, a clear change in the resistivity can be observed, this shown in Figure 2.10b for the case of the Al-10 wt.%Mg system.

### 2.3 Al-Cu-Mg alloys

While precipitation hardenable, the long aging times required for precipitation hardening in binary Al-Cu alloys, makes them impractical for commercial applications. Very early in aluminum alloy development [44], it was found that small additions (as small as 0.5wt.%) of Mg could enhance both the kinetics and maximum strength achieved in Al-Cu alloys. Moreover, adding Mg also increases the strength of the alloy in the solid solution state. Such Al-Cu-Mg alloys serve as the basis of the majority of the of the commercial AA-2XXX series of aluminum alloys [18]. The majority of studies performed on Al-Cu-Mg alloys have been on alloys with a Cu concentration higher than the Mg concentration, this resembling the typical 2XXX commercial compositions, which contain a concentration between 2 to 7 wt. % of Cu, and 0.2 to 2 wt. % of Mg [18]. This range in compositions can result in different stable phases, these shown in the phase diagram
in Figure 2.11. The S phase possess an orthorhombic structure, having a composition \( \text{Al}_2\text{CuMg} \) [18]. The \( \theta \) phase is the same as the one described in the Al-Cu section, and the T phase has been reported to have a cubic structure, with a composition \( \text{Al}_6\text{CuMg}_4 \) [30].

![Figure 2.11: Al-rich corner of the Al-Cu-Mg phase diagram at 200 °C][45]

As noted above, additions of as little as \( \sim 0.5 \) wt.% Mg are enough to cause a dramatic change in the kinetics of age hardening and maximum strength that these alloys can achieve during artificial aging (Figure 2.12). The most drastic effect caused by the addition of Mg is the rapid increase in hardness during the first seconds of artificial aging (Fig. 2.12). The magnitude of this ‘rapid hardening response’ depends on the proportion of alloying elements, but can contribute up to 70% of the peak aged hardness [46]. The initial rapid hardening is followed by a plateau of the observed hardness, subsequently evolving towards a second hardening regime, leading to the peak strength of the alloy.

Despite the large body of literature devoted to the study of precipitation in Al-Cu-Mg alloys [48], the origin of the ‘rapid hardening response’, the sequence/composition/crystallography of phases formed (particularly at short aging times), the role played by defects (vacancies and dislocations in particular), are still topics currently debated [47–52].

Focusing on compositions where the stable phases fall in the \( \alpha+S \) phase field, the first proposed sequence of decomposition was made by Bagaryatsky [53, 54], using single crystal X-ray diffraction, as,

\[
\alpha_{ss} \Rightarrow \text{zones(GP)} \Rightarrow S'' \Rightarrow S' \Rightarrow S
\]

Where the defined zones were characterized as analogous as the GP zones described above, while the \( S'' \) and \( S' \) where defined as distorted version of the S phase, having different degrees of coherency with the matrix.
Figure 2.12: Hardness evolution vs. time, aged at 200°C. Concentration are given in at.%. after [47].

Silcock, using single crystal X-ray diffraction, questioned the existence of the $S''$, proposing the following sequence [54],

$$\alpha_{ss} \Rightarrow GPB \Rightarrow S' \Rightarrow S$$

This was the first description of the Guinier — Preston — Bagaryatsky or GPB zones, these being cylinders elongated in the $<100>_a$ directions (diameter between 1-2 nm, and aspect ratio $\sim 4$), having a face centered tetragonal crystal structure [54], and being responsible for initial rapid hardening behavior. Furthermore, Silcock proposed the presence of a new phase GPB-2, following the precipitation of the previously defined GPB zones, this during artificial aging at higher temperatures (240°C) [54].

These previously proposed precipitation sequences have laid the basic nomenclature used in later research in Al-Cu-Mg alloys. Despite using the same nomenclature, very different descriptions of the chemistry and crystallography of the transition phases, sequence during precipitation, and the final effect in the strength of the material, have been proposed.

Reports of rod and lath shaped $S$ phase, having different lattice parameters, and orientation relationships, resulted in more complex interpretations of the characteristics of the $S''$ and $S'$ phases preceding a stable $S$ phase [45, 55–57]. Styles et al. [45] have been able to provide a higher insight on the variations of $S$-Phase found in literature. Using synchrotron light source X-ray diffraction, in addition to Rietveld refinement, they were able to show that the source of the multiple interpretations of the $S$-phase, is the co-existence of two $S$-phases variations, with slightly different lattice parameters. The $S1$ and $S2$ phases (in their terminology), the former is a lath-shaped, while the latter is a rod-shaped. The $S2$ phase has tendency of grow at the expense of the $S1$ phase, making it the more stable phase.

The definition of the $S''$ and GPB-II phase has been more controversial. Wang et al. [58, 59] reported them as being the same phase, having an orthorhombic structure, and a composition defined by
Al_{10}Cu_{3+x}Mg_{3-x}. This interpretation and terminology was rejected by Kovarik et al. [57] who identified the S” phase as what above has been termed S1 phase. Similarly, Rachev et al. [60] identified a quick formation of S” phase along dislocations, using electron diffraction. Kovarik et al. [61] pointed out that Rachev’s diffraction pattern interpretations were incompatible with the previous descriptions of this phase (e.g. Charai et al. [62]), instead interpreting the diffraction patterns to be what they termed GPB-II zones, having a L1_0 crystal structure. Charai et al. [62], using electron diffraction, identified the S” phase as having a monoclinic crystal structure, while no GPB-II zones were identified. Remarkably, a full overlap of GPB zones, S”, S’ and S phases was identified in their research. They proposed that the S” phase consists of an agglomeration of monolayer GPB zones, which showed no further transition to a S’ or S phase.

With regards to the GPB zones, Silcock’s early findings have been generally confirmed by later studies, using HRTEM, HAADF-STEM and APT characterization techniques [8, 62, 63]. The GPB zones have been confirmed to be cylinders elongated in the <100> α directions (diameter between 1-2 nm, and aspect ratio ~ 4). Furthermore, Charai’s [62] idea of a continuous transformation and overlapping transition of phases, has been recently supported by the HAADF-STEM and DFT calculations done by Kovarik et al. [8, 49, 64]. These authors proposed a progressive block addition theory, to explain the different structural arrangements of GPB zones observed in their experimental work. They proposed that the GPB zones were constituted by the agglomeration of basic crystal units (Figure 2.13 A)), termed 1D-GPB^1. These units can stack along the long dimension (L dimension Figure 2.13 B)), to form the observed rod-like particles. These 1D-GPB^1 units can further bond with other 1D-GPB^1 units, forming what they termed 1D-GPB^x units ((Figure 2.13 B) and C), w direction), where x is the number of zones clustered, reproducing the experimentally observed GPB zones. In their first calculations [49, 64], a stoichiometry defined as \((Mg_{2x+2}Cu_{2x+2}Al_{3x-1})\) for the GPB zones was proposed, with the possibility of an evolving stoichiometry during their formation [49].

For Kovarik et al. to observe GPB zones by HRTEM, very long aging was required (i.e. 24 hrs. at 180 °C [8]). More recent studies have focused more on identifying the microstructure corresponding to short aging times, these being responsible for the rapid initial increase in strength shown in Figure 2.12. It has been these recent studies, primarily using atom probe tomography, that have caused a reconsideration of the originally proposed precipitation processes [54], to include the effect of so-called ‘co-clusters’ on aging.

As a brief introduction to the technique, given its importance later in the thesis, atom probe tomography (APT) is a combination of field evaporation, time-of-flight spectroscopy, and position sensitive detection measurements [65, 66]. By applying a high electric field, or a combination of high electric field with a pulsed laser, to a sample with a sharp needle (tip) geometry, field evaporation of atoms occurs [65]. A constant high voltage applied between sample (positive) and detector (negative) leads to ionization of surface atoms, and a reduced energy barrier for evaporation. To evaporate, a pulsed electric field or pulsed laser is used. The ion is accelerated toward the detector, where it is collected. The chemical identification of the evaporated ion is done by means of Time-of-flight spectroscopy, this based on identifying the mass to charge ratio \(M = \frac{m}{n}\) for the species, while a projection model for the ion trajectory allows for its location within the needle to be estimated. For more details, the interested reader is referred to the recent reviews in [65, 66].

Using APT, Ringer et al. [67] observed a preferential clustering of Cu and Mg atoms (co-clusters) in the
solid solution preceding the formation of other distinct phases (e.g. GPB zones). They identified that rather than a distinct phase, such ‘co-clusters’ are a form of non-random solid solution with each cluster being comprised of between 3 and 20 solute atoms. On this basis, Ringer et al. have referred to the strengthening arising from such clusters as an "exaggerated form of solid solution hardening" [68]. Since this early work, there have been several detailed APT studies of clustering/GPB zone formation in Al-Cu-Mg alloys [47, 63, 69–71]. Marceau et al. [47] provided detailed, quantitative information in terms of number density, size and composition evolution of solute clusters in model Al-1.1 at.%Cu- x at.%Mg alloys, with x=0.2,0.5 and 1.7 at.% Mg.

Marceau et al. [47] were able to further characterize these co-clusters, immediately after quench, and after artificial aging for 60 seconds and 60 minutes at 150 °C using APT. These clusters were found to be part of a continuous distribution of features ranging in size, from as few as 2 atoms up to tens of atoms, depending on the aging time. The number density of clusters were of the order of $10^{24} m^{-3}$. In the alloys and aging conditions used, no GPB zones were reported. Based on their cluster analysis, they considered that clusters, with high Mg:Cu ratio, produced a larger strengthening effect in the alloy. Sha et al. [63] analyzed a commercial AA2024 alloy, during artificial aging at 170 °C for 30 min., 80 hrs. and 114 hrs., providing similar results as Marceau et al. [47], in terms of size and number density of the identified co-clusters. After 30 minutes of aging, the average cluster contained 90 at.% Al, with Cu and Mg concentrations of 4.5 at.% and 4 at.% respectively. These clusters were comprised of an average of 24 atoms. Additionally, they revealed a progressive transition from clusters to GPB zones, to S phase at peak aging, showing the co-existence of these different features during aging, this supports the observation of Charai et al. [62].

Additional characterization techniques have been used to provide additional support for the above interpretations. For example, Positron Annihilation Spectroscopy (PAS) has been used to help interpret the microstructural changes on aging [47, 72]. By measuring the time for the annihilation of positrons in a sample containing defects (e.g. vacancies, grain boundaries and dislocations) relative to the decay time in a perfect crystal one can provide an estimate of the density of these defects [47, 72]. This technique has been
shown to be particularly useful for characterization excess vacancies which can accelerate diffusion [9, 17], and aid in the early stages of clusters [72–74] and GP zones [9]. The complimentary Coincidence Doppler broadening (CDB) technique provides information regarding the electronic environment associated with the annihilation process. This has been used in these alloys to estimate the local composition of solute clusters under the assumption that vacancies (which are annihilation centers) are part of the clusters [72]. The study of Marceau et al. [47] showed a progressive formation of solute atom clusters around vacancies. This was further supported by showing that the estimated vacancy concentration was of the same order of magnitude as the number density of detected clusters in their system.

![Figure 2.14: Solute concentration in precipitation distribution after artificial aging for 80 hrs. at 170 °C in a AA2024 alloy.](image)

Deschamps et al.[46], in an effort to obtain results from a more statistically representative technique, employed nuclear magnetic resonance spectroscopy (NMR) and small angle x-ray scattering (SAXS) to study a model Al-Cu-Mg system. The NMR results revealed the quick formation of a Cu rich-secondary phase in the first minutes of aging at 200 °C, this signal remaining stable even after the appearance of additional signals associated with other transition phases. The SAXS experiments revealed an isotropic spectrum at low scattering angles characteristic of small particles having an ill-defined crystallographic structure (compared, for example to ordered precipitates). This result supports the interpretation of the rapid hardening being a consequence of co-cluster formation at the beginning of aging at 200 °C. Further aging caused an anisotropic streaking in the diffraction pattern, this being characteristic of features having an aspect ratio greater than one. This observation was interpreted as evidence for the formation of S (or related) phase. Combining the results of NMR and SAXS analysis led to the interpretation that the first phase to precipitate consisted of particles having a size of 4.5 Å (~25 atoms) and a composition of approximately 35% (±10%) Cu. This Cu concentration agrees with the CDB measurements of Marceau et al. [47], but is higher than the concentration measured by APT from Sha et al. [63].

The interpretation of the characteristics of the previously described co-clusters, as well their association to the rapid hardening effect, have been challenged by Zahra et al. [75, 76], Reich [50], and more recently by Kovarik et al. [8, 49]. These latter studies considered that the APT observations of co-clusters, are in fact GPB zones, specifically the 1D-GPB structure proposed above (Figure 2.13 A).
Despite these different interpretations, it appears to be widely agreed now that the initial hardening effect is due to the formation of co-clusters [70], while the later hardening arises mainly from a combination of clusters, GPB zones, and S-phase (Figure 2.14). Finally, it is the evolution of the fractions of these different phases that gives the peculiar hardening curve shown in Figure 2.12.

2.4 Al-Mg-Cu alloys

While the 2XXX series Al-Cu-Mg alloys described above are well established commercially, there has been only exploratory interest in alloys with low Cu to Mg ratios, this dating back to the late 1980’s e.g. [77]. For the purposes of this thesis, these Cu lean/Mg rich alloys will be referred to as Al-Mg-Cu alloys so as to distinguish them from the high Cu/low Mg 2XXX series alloys. Specifically, Al-Mg-Cu alloys are defined here as aluminum alloys containing $\geqslant$ 2wt. %Mg and $\lesssim$ 1wt. %Cu.

As mentioned in the introduction, the original interest in these Al-Mg-Cu alloys was to reduce softening of wrought 5XXX series Al-Mg alloys, particularly during the automotive paint bake heat treatment ($\approx$185 °C during 30 min [78]). The intent was to use the small Cu additions to trigger precipitation and thus to induce some combination of precipitation hardening and/or a reduction in recovery [6, 77, 79]. Figure 2.15 shows that such small Cu additions can be used to suppress softening, and even lead to hardening during simulated paint bake treatments in modified wrought Al-Mg alloys [6, 80]. Despite these results, it is still not understood what proportion of the change in strength in these cases arises from precipitation hardening and what proportion comes from softening due to dislocation recovery.

![Figure 2.15: Aging behavior of Al-3.35at.%.Mg-0.25at.%.Cu (Al-3wt.%Mg-0.6 wt.%Cu), Al-3.35at.%Mg-0.08at.%.Cu (Al-3wt.%Mg-0.2 wt.%Cu) alloy, and AA5754 system (Al-3.35at.%Mg) at 180 °C, following a pre-strain of 10%. These are conditions similar to those experienced in a paint bake cycle](image)

[6]
Like the Cu-rich 2XXX series alloys, Al-Cu-Mg alloys have been shown to also exhibit the ‘rapid hardening response’ upon low temperature aging. Figure 2.16 shows the evolution of tensile yield strength of a solution treated then aged (180°C) Al-4.2wt.%Mg-0.6wt%Cu alloy [60]. The initial jump in yield strength (~30 MPa) seen comparable to that seen in the high Cu/low Mg alloys (Fig. 2.12). Unlike the 2XXX series alloys, however, the Al-Mg-Cu alloys show a slow and steady increase in yield strength to peak strength, rather than a plateau followed by second hardening peak [8, 60]. Overall, the peak strength achieved in the Al-Mg-Cu alloys is generally lower than what can be achieved in 2XXX series alloys.

![Figure 2.16: Al-4.2wt.%Mg-0.6wt%Cu yield stress evolution vs time, aged at 180°C.](Image)

Referring back to Figure 2.11, the Al-Mg-Cu alloys as described above fall within the $\alpha + T$ or $\alpha + S + T$ regions of the phase diagram at 200°C. The $T$ phase is much less well studied than the $S$ phase [30, 81, 82]. This phase has been reported to be a cubic structure, with a composition Al$_6$Cu$_4$Mg$_4$ [18, 30], or a isomorphous with the T phase in Al-Zn-Mg alloys with high Mg concentration, having a body-centered cubic structure, a complex unit cell composed by 161 or 162 atoms, and a stoichiometry defined as Mg$_{32}$(Al, Zn)$_{49}$ [81]. Surprisingly, considering the established phase diagram, reports of the $T$ phase have only been made in Al-Mg-Cu alloys containing additional micro alloying elements e.g. Au [81, 83], after prolonged aging. Rather, TEM and HRTEM observations have revealed the presence of GPB zones and S-phase, similar to long time aged Al-Cu-Mg alloys. [6, 8, 61, 84–86].

In comparison to the heavily studied Al-Cu-Mg alloys (see previous section) there have been very few studies of the precipitation sequence in Al-Mg-Cu alloys. Based on TEM/HRTEM and DSC analysis (Figure 2.17) [8, 60, 61], it has been suggested that the Al-Mg-Cu alloys share the same basic precipitation sequence as observed in 2XXX series alloys. For example, the experiments and observations used by Kovarik et al. [8, 86], to support GPB zones as being responsible for rapid hardening in 2XXX series alloys, were actually performed on Al-Mg-Cu alloys. Consequently, the same controversies surrounding the nature of solute clusters/GPB zones, and S-phase variants, exists in the low Cu alloys as do in the Al-Cu-Mg alloys.
2.5 The interaction between deformation and precipitation in aluminum alloys

In the prior sections the focus has been on precipitation in a ‘well annealed’ material containing a low dislocation density. In the case of bake hardening, one has to consider how i) the presence of deformation induced defects, dislocations and vacancies, influence precipitation and ii) how precipitation can influence the process of recovery. Recovery and precipitation are highly coupled to one another making interpretation of the evolution of mechanical response in paint baked alloys complex. As noted above, the proportion of recovery induced softening and precipitation hardening in the response of the Al-Mg-Cu alloys, shown in Figure 2.15, remains unknown.

2.5.1 The effect of deformation on precipitation

Pre-deformation affects precipitation in two key ways i) it changes the thermodynamic driving force for precipitation and ii) increases the kinetics of diffusion. These phenomena have been discussed in detail in previous reviews, the interested reader being pointed to the classic work of Larch [87] and the more recent review focused on aluminum alloys by Hutchinson [88]. Here, a brief overview of the key ideas will be given.

Dislocations are generally considered to be preferred nucleation sites for precipitates, this being attributed to their effect on lowering the energy barrier for nucleation. The original model explaining this effect comes from Cahn [89], who envisioned an extra driving force for precipitation due to the relaxation of part of the dislocation’s elastic strain energy within an incoherent precipitate. This was generalized by Larch [9, 87], and the concept has been widely applied in the context of classical nucleation theory (see e.g. [9, 31, 90]). Simplified approaches take the energy barrier to be simply an adjustable fraction of that required for homogeneous precipitation, this fraction being used to obtain correct nucleation kinetics (see e.g. Perrand et al. [91]). When taking this approach, one must also adjust the number density of nucleation sites to make them proportional to the dislocation density [31, 91, 92].

A less cited, but potentially important effect of dislocations on precipitation, comes from the fact that solute will segregate to dislocations due to the elastic interaction between solute and dislocation stress field [93]. Xiao and Hansen [94, 95] developed a model to explain their observation of preferential precipitation of Ni$_3$Al, on dislocations in Ni based alloys. Using classic thermodynamic arguments, coupled to predicted Al segregation towards the region surrounding an edge dislocation, they showed how segregation could reduce the critical nucleus size to zero close to the core of the dislocation. This work has been re-investigated recently using numerical modeling involving phase field and atomistic models [96–98].

Deformation also affects precipitation by accelerating diffusion. This can occur due to the presence of an excess density of deformation induced vacancies [99–102], and by ‘short circuit pipe diffusion’ along dislocations [14, 22, 103].

For aluminum alloys, it is the diffusion of substitutional alloying elements that determines the rate of nucleation and growth of precipitates. Diffusion in this case is the result of vacancy migration, the rate
of diffusion of the solute elements being proportional to the concentration of vacancies [14]. The process of plastic deformation leads to vacancy formation due to (among other processes) the dragging of jogs on dislocations [104]. Some phenomenological models for vacancy production during deformation have been developed based on such mechanisms [105, 106]. Upon aging, this ‘excess’ density vacancies will decay towards the equilibrium concentration at the aging temperature, this due to vacancies annihilating on grain boundaries, dislocations, or by the condensation of vacancies into dislocation loops [99, 100, 107–109]. Evidence of the importance of vacancies for the formation of precipitates is often cited in the form of precipitate free zones around dislocations and grain boundaries, arising from the depletion of vacancies and solute in the regions around them [110, 111]. Thus, the direct effect of vacancies on accelerating diffusion is usually limited to the early stages of aging before reaching equilibrium [100, 101].

So-called “pipe diffusion” of solute along the core of dislocations [14] has also been cited as a reason for accelerated nucleation and growth of precipitates in deformed samples [22, 103, 112]. This faster path for solute diffusion is considered to require a lower activation (0.6 to 0.7 of the energy required in bulk diffusion [113]), having a significant effect at lower temperatures [14]. This diffusive mechanism has been used to support dynamic strain aging, where large concentration of solute are necessary to justify this effect [114]. The experimental complexity to study this type of diffusion have encouraged the use of computer simulations [113, 114], supporting the need of pipe diffusion as a fast diffusing path, but also showing the potential need of vacancies for this process to take place [113, 114].

The combination of the thermodynamic and kinetic effects described above has observable consequences on the kinetics of precipitation, precipitate size [34, 115], precipitate size distribution [34, 111] and the precipitation sequence [103, 111].

For Al-Cu-Mg and Al-Mg-Cu alloys, it has been reported that a deformed microstructure leads to the direct formation of the S-phase along dislocations [60, 116]. The influence of vacancies and dislocations have also been observed in non-deformed samples, due to dislocation loops formed by quenched-in vacancy agglomeration, these being the sites for rapid and preferential formation of the S-phase [45, 50, 60, 116]. Ratchev et al. [84], used DSC to monitor the sequence of precipitation in a Al-4.2 wt.% Mg- 0.6 wt.% Cu alloy that had been solutionized, then deformed in tension to 2% and 5% strain. As can be seen in Figure 2.17, the sharp exothermic peak associated with the precipitation of co-clusters/GPB zones in the as-quenched sample (peak A, Figure 2.17), was observed to broaden and shift to higher temperatures with increasing deformation. At the same time, the peak attributed to the S-phase was seen to shift towards lower temperatures. This has strong similarities to DSC results arising from deformed and aged 2XXX series alloys [115].

The effect of dislocations on solute cluster formation in an Al-3.6 wt.%Cu-1.6 wt.%Mg alloy has also been studied using electrical resistivity and APT measurements [117]. These experiments were performed on samples aged for 96 hours at room temperature after solution treatment and deformation. The results of both techniques pointed to an increasing reduction in cluster density with level of deformation. A similar suppression of clustering due to pre-strain in an Al-Mg-Si alloy has been attributed to the rapid loss of vacancies to dislocations [118, 119].
2.5.2 Recovery in the presence of precipitation

It is known that the presence of precipitates can hinder the rate of recovery in precipitation hardenable alloys, either by pinning those dislocations on which precipitates have nucleated heterogeneously [31, 120], or by hindering the glide/climb of dislocations during recovery [120].

In the model developed by Zurob et al. [31] it was assumed that precipitates act to pin dislocation segments during recovery, the probability of pinning being taken to be,

\[ P_{\text{pin}} = \frac{N(t)}{N_c(t)} \]  

where \( N(t) \) is the number density of precipitates and \( N_c(t) \approx 0.5\rho^{3/2} \) is the number density of dislocation nodes. When \( P_{\text{pin}} > 1 \) then it was assumed that recovery was completely stopped. Alternatively, when \( P_{\text{pin}} < 1 \) then the model developed by Verdier, Equation 2.3 was modified as,

\[ \dot{\sigma}_{\text{Zurob}} = \dot{\sigma}_{\text{Verdier}}(1 - P_{\text{pin}}) \]  

In the case of precipitation into a pre-deformed microstructure, \( P_{\text{pin}} = 0 \) at \( t = 0 \) but increases as precipitation takes place, this leading to the halting of recovery. Further aging, however, would lead to precipitate coarsening and a drop in \( N \) and the continuation of recovery.

The complex interrelationship between precipitation and recovery when they occur concurrently means that verifying the above equation for a variety of systems is difficult. Roumina [120] attempted to separate the effects of precipitation and recovery experimentally by preparing Al-Mg-Sc alloys containing a stable distribution of \( Al_3Sc \) precipitates, followed by deformation then a recovery heat treatment. It was found that Zurob’s approach alone was not sufficient to explain the observed recovery kinetics as it over-predicted...
the length of the stasis in recovery. In Roumina’s model [120] two parallel processes were considered to control the recovery kinetics: Standard dislocation-dislocation annihilation unaffected by the precipitates as described by Equation 2.3, and annihilation controlled by dislocations having to circumvent precipitates by climb. To capture the kinetics of the second process, Roumina adopted a simple climb based kinetic equation [121],

\[ \dot{\sigma}_{\text{Climb}} = -C \frac{1}{\sqrt{f_v}} \frac{b^2}{d_{\text{ppt}}} \frac{D_v}{kT} (\dot{\sigma})^2 \]  

(2.6)

Where \( d_{\text{ppt}} \) is the precipitate diameter, \( D_v \) is the vacancy diffusivity, \( k \) is the Boltzmann constant, \( T \) is the aging temperature, and \( C \) is a constant. It was then considered that the total rate of recovery was the sum of the rates of recovery given by equations 2.3 and 2.6 weighted by probability that a moving dislocation would meet a precipitate during recovery (\( f \)),

\[ \dot{\sigma}_{\text{Roumina}} = (1 - f) \dot{\sigma}_{\text{Verdier}} + f \dot{\sigma}_{\text{Climb}} \]  

(2.7)

Where \( f \) was defined as being proportional to the ratio of the dislocation annihilation distance to the precipitate spacing. An example of the experimental and modeling results, using the previously described model, can be seen in 2.18. Here it is observed how the effect of softening stasis (controlled by the term \( \dot{\sigma}_{\text{Climb}} \) above), due to precipitation, takes place after several hours of recovery at 190 °C.

**Figure 2.18:** Yield stress evolution during aging at 190 °C, after artificial aging (425 °C for 80 min and 8 days) and cold roll (80% reduction)

[120]

While Roumina’s work provided detailed insight into the process of recovery in the presence of a set of stable precipitates present prior to deformation, the vast majority of literature on the effect of precipitates on recovery has been on the more practically important situation when precipitation and recovery occur
concurrently. These studies are based on the effects described above, with the main objective of predicting the evolution of the strength of the material, in which these two phenomena take place during aging. The overlapping nature of precipitation and recovery, does not facilitate a clear identification of the relation between these two, leading to a multiple modeling strategies [22, 31, 111, 112, 120, 122, 123]. The selection of a specific strategy is based either on the observations made for the conditions used in the studied alloy and processing conditions, or on simplifications needed to deal with the complexity of concurrent recovery and precipitation. For the case of the Al-Mg-Cu system, under the processing conditions of the pain bake cycle, more studies to understand the relationship between these phenomena are required to develop a successful modeling strategy for coupled recovery and precipitation.

2.6 Summary

1. Small additions of Cu to Al-Mg alloys for the formation of precipitation hardenable alloys from Al-Mg alloys that are conventionally used in the wrought form.

2. Significant controversy still exists in the sequence of precipitates formed in Al-Mg-Cu and Al-Cu-Mg alloys with much of our understanding of the behaviour of Al-Mg-Cu alloys coming from studies on Al-Cu-Mg alloys

3. Most recent literature seems to point to the decomposition of Al-Mg-Cu alloys as being a gradual transition from solute clusters to the equilibrium S-phase

4. Precipitation into a deformed microstructure in Al-Mg-Cu alloys appears to accelerate the transition towards the equilibrium S-phase, with preferential formation of the equilibrium phase on dislocation.

5. The relative importance of precipitation hardening versus recovery softening (and how these two processes are related to one another) is still unknown for Al-Mg-Cu alloys subjected to paint bake operations.
Chapter 3

Scope and Objectives

It is clear that Al-Mg-Cu alloys with low Cu:Mg ratios are potentially interesting for applications where wrought Al-Mg alloys are currently being used. The ability to stop softening during aging would allow for less material usage and higher weight-savings in the automotive industry. Understanding exactly how the processes of precipitation and recovery are coupled is necessary if we are to better understand how to design such alloys for optimal utilization.

The objective of this thesis is to identify how concurrent precipitation and recovery interact in such alloys, and to relate how these processes determine the time evolution of the material’s yield strength and work hardening under simulated industrial automotive paint bake cycle conditions.

To achieve this objective, an approach combining experiments and models has been utilized. Starting from model ternary alloys, mechanical property assessment and the imposition of pre-deformation have been performed by uniaxial tensile tests performed at low homologous temperatures. Microstructural characterization has been performed at the macroscopic scale (e.g. via calorimetry and electrical resistivity), and the microscopic scale (e.g. atom probe tomography, electron microscopy). Phenomenological models for microstructure evolution (i.e. precipitation and recovery) and mechanical response (dislocation and precipitate based hardening) have then been built based on these observations.

In the first part of this thesis, the early stages of precipitation and strengthening in undeformed alloys is explored using experiments and models (Chapter 5). Having obtained an understanding of precipitation in the absence of deformation, the next chapter (Chapter 6) will examine the effect of pre-deformation on precipitation kinetics and precipitate type. Finally, the work hardening response of deformed, then aged samples will be assessed experimentally and modelled (Chapter 7). In particular, this section of the thesis aims to separate the contributions of precipitation and forest hardening to the macroscopic yield stress, and to provide guidance for future alloy development strategies.
Chapter 4

Experimental Procedures

In the following section, a description of the methodology and characterization techniques used to accomplish the previously stated objectives will be provided.

4.1 Materials

For this study three alloys were used: two Al-Mg-Cu alloys, and a Al-Mg alloy, denominated AA5252. These were provided by Novelis Global Technology Centre, our industrial partner in this project. These alloys were produced at Novelis using a Direct Chill Casting method (DC) [124]. For the Al-Mg-Cu alloys, the starting 95 mm thick DC cast material was scalped to a thickness of 77.5 mm. The material was then homogenized at 500 °C for 2 hrs., using a 50 °C/h heating rate, hot rolled (between 250 °C and 300 °C) to a thickness of 5 mm, and finally air cooled to room temperature. The Al-Mg AA5252 alloy was also scalped to a thickness of 77.5 mm, hot rolled (between 250 °C and 300 °C) up to 7mm, and cold rolled to 5mm final thickness. The previous described processes took place at Novelis and shipped to UBC. The chemical composition of the Al-Mg-Cu and Al-Mg alloys was evaluated by means of Optical Emission Spectrometry at Novelis, and is shown in Table 4.1 for the Al-Mg-Cu alloys, and in Table 4.2 for the Al-Mg alloy.

<table>
<thead>
<tr>
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<th>Mg</th>
<th>Cu</th>
<th>Fe</th>
<th>Si</th>
<th>Ti</th>
<th>Ni</th>
<th>Mn</th>
<th>Zn</th>
<th>Cr</th>
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<td>0.048</td>
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<td>0.0005</td>
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<td></td>
<td>(wt.%)</td>
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<td>0.54</td>
<td>0.1</td>
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<td>0.015</td>
<td>0.007</td>
<td>0.001</td>
<td>0.002</td>
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<tr>
<td>0.12 at.% Cu Alloy (at.%)</td>
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<td>0.046</td>
<td>0.007</td>
<td>0.003</td>
<td>0.0005</td>
<td>0.0012</td>
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<tr>
<td></td>
<td>(wt.%)</td>
<td>2.96</td>
<td>0.28</td>
<td>0.1</td>
<td>0.05</td>
<td>0.014</td>
<td>0.007</td>
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<td>0.003</td>
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Table 4.1: Composition obtained by OES of alloys studied. Balance is aluminum.
4.2 Thermo-Mechanical Treatments

The previously described material was further processed at UBC to be suitable for the planned experimental procedures. The details of this processing are shown below.

4.2.1 Cold Rolling

The material received from Novelis was sectioned, and further cold rolled, at constant rolling velocity, using a laboratory rolling mill with work roll radius of 56 mm. The material was rolled following the rolling direction of the as-received material, to a final thickness of 1 mm, without lubrication. The reduction steps where calculated using Equation 4.1 [125],

$$
\Delta = \frac{H_f}{\sqrt{R(H_0 - H_f)}}
$$

(4.1)

where $R$ is the radius of the work roll, $H_0$ is the initial thickness, and $H_f$ is the final thickness after the rolling pass. The calculated $\Delta$ parameter should be smaller than one to insure the same strain distribution through the sheet thickness. Based on this calculation, 15 steps with a reduction per pass of 10% was used to achieve a total reduction of 80%. An average value of $\Delta = 0.5$ was calculated.

4.2.2 Solution Treatment and Recrystallization

The cold rolled sheet was subjected to a heat treatment with the dual purpose of recrystallizing the material and to produce a super saturated solid solution in the Al-Mg-Cu alloys. The solution/recrystallization treatment was performed in a salt bath (60% potassium nitrate + 40% sodium nitrite), held at 550 ± 2 °C, with immediate quench in water at room temperature (quench rate of ≈190 °C/s, measured experimentally with a thermocouple attached to the center of a sample). The solution treatment was selected using Thermocalc (TTAl 6 database), considering the composition of the Al-Mg-Cu system with 0.23 at.% Cu (Table 4.1). The calculations revealed Aluminum $\alpha$ matrix and Al$_3$Fe, as the only equilibrium phases present at the chosen temperature. The time for the solution/recrystallization treatment was selected based on a balance between attaining the desired solid solution state in the material, and obtaining a fully recrystallized material with a grain size convenient for the further analysis. The solid solution state was verified by resistivity measurements (details below), revealing no further increase of resistivity after 10 min of solution treatment, using this time for the further solution/recrystallization treatments used in the Al-Mg-Cu systems. Thus, the same solution treatment has been used previously for a Al-Mg-Cu alloy [8]. The grain size was measured by

<table>
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<th>Mg</th>
<th>Cu</th>
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<th>Mn</th>
<th>Zn</th>
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<td>0.23 at.%Cu Alloy (at.%)</td>
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<td>0.0008</td>
<td>0.031</td>
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<td>0.005</td>
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</table>

Table 4.2: Composition obtained by OES of high purity AA5252 alloy. Balance is aluminum.
mean by line intercept method using optical microscopy, revealing an average grain size of 56 µm in the Al-Mg-Cu alloys. For the case of the AA5252 alloy, the objective of the heat treatment after cold rolling, was to achieve full recrystallization of the alloy, and to achieve the same grain size as that in the Al-Mg-Cu alloy. This was done in the same salt bath as described before, holding the material at 500 °C for 1 minute, followed by immediate water quench, resulting in an average grain size of 41 µm.

4.2.3 Aging treatments
All aging treatments were made in a silicone-based open oil bath, coupled to a mechanical stirrer, except for samples where aging was longer than 420 min, where a box furnace was used. The temperature was controlled using a k-type thermocouple connected to an electronic controller (PID controller), with a temperature variation of ±2 °C. After aging treatment, all samples were quenched in water, and stored in liquid nitrogen.

4.2.4 Tensile Test
Uniaxial tensile tests were used as a means to mechanically characterize the material, as well as to apply a controlled level of deformation in all samples where pre-deformation was done before aging. Tensile samples were machined out of the cold rolled material (see above), having the geometry shown in Figure 4.1.

These tensile samples where further recrystallized/solution treated using the methodology described above. Tensile tests were performed using a Instron screw driven machine equipped with a 5 kN load cell. The tests were performed at a constant strain rate of $10^{-3}[1/s]$, at a temperature of 77K to avoid the effects of dynamic strain aging [37, 125, 126]. In order to achieve this temperature for the tensile test, the sample and sample holder arrangement was immersed in liquid nitrogen using a thermal container. The setup was allowed to equilibrate at 77K for ~5 min, until excessive boiling of the liquid nitrogen ceased. The strain was measured using a MTS extensometer model 63211C-21, directly attached to the sample. The displacement
measurements were converted to strain. The true stress vs true strain was used to calculate yield stress (0.2% strain offset). The work hardening rate was obtained by numerical differentiation (The original data was smoothed using a Savitzky-Golay filter, using a window of 23 points and 3 degree polynomial, the numerical derivative was evaluated from this smoothed data).

4.3 Characterization

4.3.1 Optical microscopy

Microstructural observations were performed using optical microscopy with the objective of measuring grain size. In order to do this, a standard metallographic procedure was used. First, rough mechanical polishing was done using the following sequence of ANSI grits for grinding papers: 300, 400, 600, 800, 1200. After the last rough mechanical polishing, fine polishing was done using 1 µm diamond based colloidal compound. The grains were revealed using etching and anodization techniques for the Al-Mg-Cu alloys, and for the Al-Mg alloy respectively. The etching was done by dipping the polished samples in Keller’s etchant (2.5 % vol. nitric acid, 1.5 % vol. hydrochloric acid, 1 % vol. hydrofluoric acid, balance distilled water) for 35 seconds. The anodization procedure was done using Barker’s anodizing solution (2.5% vol. fluoroboric acid, balance distilled water), using a direct current source operating at 30 V for 60 to 120 seconds and 99.9% purity Al as a cathode. Finally, the observations were done using a light microscope with a polarized light filter.

4.3.2 Scanning Transmission Electron Microscopy in Scanning Electron Microscope

These observations were possible by using a thin sample, as the type of sample standard for Transmission Electron Microscopy (TEM), allowing electron transmission through its cross section (Usually using the available standard maximum acceleration voltage available in SEM of 30 kV).

Sample preparation was done following the same available procedures used to produce TEM samples. This was done by mechanically grinding the sample to a thickness between 20 to 50 µm. This thin sample was sectioned into 5 mm in diameter discs, using a disc punch device. The resulting samples were further electropolished using a Struers Tenupol-5 twin jet polisher system, operating at 30 V, using 1/3 total volume of nitric acid (HNO₃) with 2/3 methanol (CH₃OH) as electrolyte, this at -20 °C. Samples were observed using a FEI Versa dual beam system operating at an acceleration voltage of 30 kV, operating the STEM detector in bright field mode.

4.3.3 Electrical Resistivity

Electrical resistivity changes have been used as a mean to track the evolution of microstructure during aging. This is performed by measuring the change in resistivity from the solid solution state, and as a function of aging time [127]. The electrical resistivity measurements were done by measuring resistance of the material at 77K in a liquid a nitrogen bath, using a custom made four-point probe resistance bridge with an applied
current of approximately 20 mA, and a reversion frequency of 30 Hz [128].

The calibration of the system was verified using a pure (99.99%) aluminum sample. Conversion of resistance to resistivity was done using the following expression,

$$\rho = \frac{A}{LR}$$

(4.2)

where $A$ is the cross section area of the sample, and $L$ is the length between the inner electrodes.

The resistivity measurements were done directly on the tensile samples described above, tracking resistivity in the different states of the material (i.e. solid solution, aged, pre-deformed, and pre-deformed+aged) taking advantage of the selected geometry of the gauge section, allowing measurements before and after deformation, using the results of the tensile test measurements to calculate the change of the cross-section area. The reported measurements were product of the average measurements for samples subjected to the same conditions. For error calculation, calculation of uncertainty for Equation 4.2 was done, this assuming each term to be independent [129],

$$\delta \rho = \sqrt{(\frac{\partial \rho}{\partial A} \delta A)^2 + (\frac{\partial \rho}{\partial L} \delta L)^2 + (\frac{\partial \rho}{\partial R} \delta R)^2}$$

(4.3)

Where the error associated to each independent value ($\delta x$), was assumed to be the standard deviation resulting from 12 measurements, this for each independent variable.

### 4.3.4 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a classic technique to detect and potentially quantify phase transformations. This technique relies on a precise measurement of the heat evolving from, or absorbed by, a sample when a phase transformation takes place in it. Formation of a secondary phase will result in the emission of heat out of the sample, while a phase dissolution will absorb heat to take place.

For the results shown in this work, a TA Instruments model Q2000 system was used, using a scanning window ranging from -50 up to 350 °C, at a 5 °C/minute heating rate. The studied samples were solution treated material, cut in square sections of 5 mm by 5 mm. The material subjected to pre-deformation was obtained from the gauge section of the pre-deformed tensile sample. Samples were analyzed in high purity aluminum baskets, using a basket of same characteristics for the reference sample. The baseline was obtained by performing two scanning cycles as defined above. The second cycle was used as a baseline from the first cycle, where the thermal signals associated to precipitation take place, under the assumption that no further precipitation occurs after the first thermal cycle. This methodology was adopted after Ivanov [130].

### 4.3.5 Atom Probe Tomography

Samples studied in this work were aged 20 and 160 minutes at 200 °C, this after solution treatment, and after 10% pre-strain. The previously described material was sectioned to obtain "matchsticks", these consisting of square prisms with a square section of ~500 µm width, and 45 mm length. These were subjected to a
2-stage electrochemical polishing technique employing perchloric acid (HClO₄), to produce "needles" with a section between 50 to 150 nm of diameter [65]. A Cameca LEAP 5000 XS system was used to obtain the APT data for this work’s analysis. The system was operated at a base temperature of 50K, using a pulsing high-voltage at 20% increase of the standing voltage. The DC voltage was progressively adjusted to maintain a detection rate of 1 ion per 100 pulses.

The obtained dataset was analyzed by means of isosurface analysis to reveal fluctuations in concentration that can reveal clusters. the dataset is divided in blocks with an specific composition. These previously defined blocks will be single out by a user selected concentration. The addition of adjacent blocks with result in three dimensional volumes, these called isosorfaces. One-dimensional concentration profiles were also employed. These consist on using a cylinder or cuboid extended in any selected direction of the reconstructed volume, resulting in a compositional profile along this axis. The 1D profiles were defined in the cross-section of the identified volumes by isosurface analysis [65]. The estimate of the error for these profiles is defined as $\sigma = \sqrt{\frac{c_i(1-c_i)}{n_i}}$, where $c_i$ is the measured concentration of the element i, and $n_i$ is the number of atoms i detected in the selected bin [131].

### 4.3.6 Summary of Conditions Tested

Table 4.2 summarizes all of the conditions tested after solution treatment and aging. Table 4.3 shows all conditions tested after solution treatment, pre-deformation and aging.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Aging time [minutes]</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>160</th>
<th>180</th>
<th>420</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23 at% Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td></td>
<td>2</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.12 at% Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.2:** Summary of samples/conditions tested without pre-deformation. The numbers correspond to the number of tensile samples tested per condition.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Pre-deformation [MPa]</th>
<th>Aging time [minutes]</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>30</th>
<th>180</th>
<th>420</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23 at% Cu</td>
<td>44</td>
<td></td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>174</td>
<td></td>
<td></td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>AAS252</td>
<td>44</td>
<td></td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>174</td>
<td></td>
<td></td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.3:** Summary of samples/conditions tested following pre-deformation. The numbers correspond to the number of tensile samples tested per condition.
Chapter 5

Characterization of Al-Mg-Cu System During Artificial Aging

As shown in Chapter 2, there is relatively little known about the early stages of aging in Al-Mg-Cu alloys having a low Cu/Mg ratio. The work reported in this chapter aims to provide a detailed characterization of the microstructure (clustering and precipitation) evolution during aging of as-solutionized samples for times and temperatures relevant to the industrial paint bake cycle. These changes will be linked to the yield strength of the material by modelling. This chapter serves as the starting point for further exploration of the more complicated process of aging of pre-deformed samples in subsequent chapters.

5.1 Results

5.1.1 Optical metallography
The results of the next sections were obtained from as-recrystallized and solid solution treated material as described Methodology section (Section 4). The characteristic microstructure is shown in Figure 5.1. It presented equiaxed grains with an average size of 56 μm, this determined by line intercept method. Large coarse particles were also identified, and deemed as constitutive particles commonly denominated as stringers which tend to align along the rolling direction. Regardless of the previously described particles, the obtained microstructure was considered appropriate for the next steps of characterization.

5.1.2 Differential Scanning Calorimetry
Differential scanning calorimetry (DSC) measurements have been widely used in the past to identify the formation and dissolution of various phases during the artificial aging of solution treated Al-Mg-Cu and Al-Cu-Mg alloys (cf. Figure 2.17). Though non-isothermal DSC has its limitations [127], it is valuable as a first, simple, way of identifying temperature ranges were different reactions may take place. Here, DSC is used simply to confirm that distinct reactions can be observed for solute clustering, cluster dissolution and
equilibrium phase formation [60, 132]. Figure 5.2 shows the thermogram corresponding to starting from a solutionized state\(^1\) (Section 4.2.2) with the Al-3.23 at.% - 0.23 at.%Cu alloy, the measurement being made at a constant heating rate of 5 °C/minute. In this figure an exothermic peak is observed in the temperature range \(\approx 75°C - 150°C\) (peak A in Figure 5.2). This has been previously associated with the formation of clusters and/or GPB zones in similar alloys [60, 132]. At temperatures above \(\approx 200°C\), a sharp endothermic peak (peak B) is observed, this being generally associated with the dissolution of the clusters/GPB zones [60, 132]. Finally, a second exothermic peak (Peak C) is observed at temperatures above 300°C, this one consistent with previous reports of S-phase formation [60, 132]. The endothermic peak at the beginning of the thermogram (Peak E), has been associated to an artifact of the measurement and should not be considered as characteristic of the material. In the sections that follow, the results of isothermal aging at 160°C and 200°C will be presented for aging times ranging from 2 minutes to several hours. The results in Figure 5.2 suggest that we should expect the formation of clusters/GPB zones at short times, with the possibility of their dissolution and possible formation of more stable phases upon longer aging time.

5.1.3 Mechanical Behaviour of Artificially Aged Al-Mg-Cu Alloys

The decomposition of the solid solution during artificial aging of the Al-Mg-Cu alloys is expected to lead to changes in mechanical response. Figure 5.3a shows how the stress-strain curves measured at 77 K evolve with aging at 200°C for the Al-3.23 at.% - 0.23 at.%Cu alloy \(^2\). The results in Figure 5.3a show that the yield strength rises rapidly from 87 MPa to 150 MPa within the first 2 minutes of aging. This is followed by a gradual but continuous increase of the yield strength over the following 18 hours (1100 min). Nearly identical results are obtained for aging at 160°C (Figure 5.3b). For the case of Al-3.2 at.%Mg-0.12 at.%Cu alloy, generally lower stress values are observed, compared to the ones of Al-3.23 at.% - 0.23 at.%Cu alloy, for the same aging time and temperature.

---

\(^1\)Between solution treatment and test, a period of about 1 hour at room temperature took place for sample preparation

\(^2\)Note that only select conditions are shown in Figure 5.3. The full set of data can be found in Appendix A.
Figures 5.3a and 5.3c suggest a minor change to the work hardening behaviour of the material, after 180 minutes at 200°C, while the material aged at 160°C (Figure 5.3b), does not show any change, even after 420 minutes of artificial aging. This can be seen more clearly if the stress-strain data is plotted as a Kocks-Mecking plot (work hardening rate versus flow stress minus yield stress, Figures 5.4). The lack of change in work hardening rate at early aging times (<160 minutes), in the samples aged at 200°C (Figure 5.4b and 5.4c), and during the whole selected aging period in samples aged at 160°C, is particularly notable as it suggests that the hardening phase(s) are predominantly small and shearable, a point that will be discussed in more detail below.

Given the lack of strong change in work hardening rate, but rather significant change in yield strength, it is worth investigating the time, temperature and composition dependence of the yield strength evolution more closely. Figure 5.5 presents the 0.2% offset yield strength evolution for the 0.23at.%Cu and 0.12at.%Cu alloys, aged at 200°C, and the 0.23at.%Cu alloy aged at 160°C. Interestingly, the yield strength is seen to evolve at a similar rate for all conditions beyond the first 2 minutes of aging. This matches the linear evolution of yield strength with logarithmic time reported by Court and Lloyd [6] on similar alloys tested at room temperature after aging from 30 to 10000 minutes at temperatures between 140 and 200°C. Moreover, the similarity of the aging response of the 0.23at.%Cu alloy at 160 and 200°C, agrees with the results presented for similar alloys by Ratchev et al. [133]. Comparing the behaviour of the 0.12 and 0.23at.%Cu alloys, the alloy containing ~50% less Cu is able, after 30 minutes of aging, to provide a similar
Figure 5.3: Stress vs. strain evolution of Al-3.23 at.%-0.23 at.%%Cu alloy during artificial aging at a) 200 °C, and b) 160 °C, and Al-3.2 at.%%Mg-0.12 at.%%Cu alloy, at c) 200 °C. All tensile tests were done at 77K.
Figure 5.4: Kocks-Mecking plot evolution of Al-3.23 at.%Mg-0.23 at.%Cu alloy during artificial aging at a) 160 °C, b) 200 °C, and Al-3.2 at.%Mg-0.12 at.%Cu alloy during aging at c) 200 °C. The flow stress has been reduced by the yield stress measured at $\varepsilon = 0.2\%$ offset. All tensile test were done at 77K.
5.1.4 Evolution of Electrical Resistivity on Aging

Electrical resistivity has been widely used as a mean-field characterization technique in cluster and precipitation hardening aluminum alloys [127, 134, 135]. Changes in resistivity reflect both the loss of solute from solid solution and, in the case of sufficiently fine clusters/precipitates, an increase in scattering arising from phase interfaces. While disentangling the effects of solid solution and interfaces in these alloys can be challenging [136], the method gives an independent measurement for comparison against the tensile data and more local microstructural information obtained from APT or (S)TEM.

Figure 5.6 shows the change in electrical resistivity for those samples whose yield strength is shown in Figure 5.5. The higher as-quenched resistivity for the 0.23at.%Cu alloy compared to the 0.12at.%Cu alloy reflects the higher overall solute content. Consistent with the ‘rapid hardening’ behaviour illustrated in Figure 5.5, the resistivity also increases rapidly within the first 2 minutes of aging, the magnitude of the jump being much larger in the case of the 0.23at.%Cu alloy compared to the 0.12at.%Cu alloy. This rapid increase is consistent with the formation of small solute clusters that contribute significantly to conduction electron scattering (cf. results on 2XXX-series alloys [137, 138]). Following the rapid initial resistivity jump, both alloys exhibit a long period (> 100 min) of nearly constant resistivity, followed by a slow decrease for the case of samples aged at 200°C. It is notable that the resistivity evolution of the 0.23at.%Cu alloy, aged at 160 and 200°C, are nearly identical. This observation matches the nearly identical yield strength evolution.
shown in Figure 5.5.

Figure 5.6: Resistivity evolution for Al-3.23 at.% - 0.23 at.%Cu, Al-3.2 at.% - 0.12 at.%Cu alloy during artificial aging at 200°C and 160°C.

5.1.5 Microstructural Observations

Atom Probe Tomography

To investigate the microscopic origin of the observed changes in yield strength and resistivity, atom probe tomography was performed on samples taken from the 0.23at.%Cu alloy after aging at 200°C for 20 min (typical paint bake time) and 160 min of aging (end of the resistivity plateau in Figure 5.6). Ideally, one would like to compliment such local observations with other cluster/GPB zone sensitive techniques such as HR-TEM, STEM and/or SAXS/SANS to provide better statistics. However, the lack of atomic number contrast in these alloys drastically limits the options for complimentary techniques (see for example Section 2.3). This has, potentially, been the major stumbling block for previous studies on the early stages of aging in this alloy system. Figure 5.7a shows an APT volume measured on a sample aged for 20 min. Within this volume, iso-surfaces reveal a distribution of small Mg and Cu enriched particles. The one-dimensional composition plots for the selected particles reveal the particles to contain approximately 80-90at.%Al, 10-15at.%Mg and 1-5at.%Cu. Further aging to 160 min (Figure 5.7b) led to only minor changes in the composition and sizes of the particles based on iso-surface and one-dimensional composition plots. In both cases, the compositions were found to be similar to, but distinct from, those previously reported for clusters/GPB zones in an AA2024 alloy (4.3 wt%Cu, 1.3wt%Mg) [63].
Figure 5.7: Atom probe volumes measured on samples aged for a) 20 min and b) 160 min at 200°C. In each case, iso-surfaces corresponding to a) 3.13 atoms/nm$^3$ Mg and 0.5 atoms/nm$^3$ Cu, and b) 3.5 atoms/nm$^3$ Mg 1.0 atoms/nm$^3$ Cu are plotted to reveal the presence of small Mg and Cu rich particles. One dimensional composition plots are provided along two perpendicular directions, the results being representative of the observations made in the other particles.
Relying on conventional cluster finding algorithms has drawbacks owing to the underlying assumptions that one must make [65]. Cluster-finding methods are usually prone to parameter-selection biases [66] in particular for cases where multiple morphologies of features are present [21]. As an alternative method, a pair correlation based approach has been adopted here to interpret the results in Figure 5.7. This radial distribution function based method for extracting information on clusters and precipitates [139], and its direct relationship to the formalism conventionally used in small angle scattering, has been established [140, 141] and used recently for studying clustering in aluminum alloys by Ivanov et al. [142]. A description of the relationship between the radial distribution function, accessible from the APT datasets, and the pair correlation function is provided in Appendix C.

The pair correlation approach used here has the advantage of providing a self-consistent, parameter free description of the solute distribution within the dataset. This can then be interpreted to obtain information on particle size and composition when combined with a suitable model.

A modified definition of the pair correlation function (PCF), compared to the one introduced in [143], has been used. The form used here allows the PCF to be expressed in an equivalent way to the form used in small angle scattering in the case of an isotropic two-phase system where the composition is uniform within the two phases [140, 142, 144, 145]. The pair correlation function has been defined as,

\[ \gamma_{i-j}(r) = c_i^0 c_{i-j}(r) - c_i^0 c_j^0 \]  

where \( c_i^0 \) is the average concentration of species \( j \) in the alloy and \( c_{i-j}(r) \) is the concentration of species \( j \) at a distance \( r \) from an atom of species \( i \) averaged over all atoms of species \( i \). \( \gamma_{i-j}(r) \) is the correlation between the concentration fluctuations in element \( i \) and element \( j \), i.e. \( \langle \Delta c^i \Delta c^j \rangle \). Equation 5.1 can be written in terms of two contributions,

\[ \gamma_{i-j}(r) = \gamma_{ij}(0) \gamma_0(r) \]  

The function \( \gamma_0(r) \) is a normalized correlation function, such that \( \gamma_0(0) = 1 \) and \( \gamma_0(r \to \infty) = 0 \). The meaning of \( \gamma_0(r) \) is particularly intuitive in the case of a single object in a (infinitely) large homogeneous volume. In this case \( \gamma_0(r) \) is the normalized autocorrelation; it is the intersection volume of the object and its ‘ghost’ displaced by a distance \( r \) normalized by the object volume. For simple shapes, this function can be determined analytically. For example, for spherical particles of radius \( R \), \( \gamma_0(r) \) is [146],

\[ \gamma_{sphere}^0(r) = \begin{cases} 1 - \frac{3r^3}{4R} + \frac{r^4}{16R^3} & (r \leq 2R) \\ 0 & (r > 2R) \end{cases} \]  

In the case of randomly distributed precipitates whose radii are distributed (e.g. following a log-normal distribution) a volume weighted numerical integration of Equation 5.3 can be performed to obtain \( \gamma_0(r) \).

It is important to note that \( \gamma_0(r) \) is a unique function of the size and geometry of the second phase. The effect of matrix/particle composition enters entirely through \( \gamma_{i-j}(0) \) which is a measure of the compositional
contrast between the phases. In the case of the correlation between atoms of the same type \(^3\),

\[ \gamma_{i-i}(0) = f_v (1 - f_v) \left( c_p^i - c_m^i \right)^2 \]  

(5.4)

while in the case of the correlation between two different types of atoms we obtain,

\[ \gamma_{i-j}(0) = f_v (1 - f_v) \left( c_p^i - c_m^i \right) \left( c_p^j - c_m^j \right) \]  

(5.5)

In the above equations, \( c_p \) and \( c_m \) refer to the particle and matrix compositions, \( c_0 \) to the average compositions and \( f_v \) to the volume fraction of particles. It is important to note that if only one type of objects are present, the 3 PCFs \( \gamma_{i-i}(r) \), \( \gamma_{j-j}(r) \) and \( \gamma_{i-j}(r) \) should all be proportional, the factor of proportionality being related to the fraction of objects and the composition contrast. Moreover, based on the definitions given above,

\[ \gamma_{i-j}(0) = \sqrt{\gamma_{i-i}(0) \gamma_{j-j}(0)} \]  

(5.6)

In the present case, we have calculated the Mg-Mg, Cu-Cu and Mg-Cu pair correlations (Figure 5.8) from the APT data shown in Figure 5.7. If the particles observed in Figure 5.7 belonged to a single population with a uniform composition, then all three pair correlation functions should be proportional to one another. Figure 5.9 shows the normalized Mg-Mg, Cu-Cu and Cu-Mg pair correlations revealing that this can’t be true as the correlation length for the Cu-Cu and Cu-Mg pair correlations are noticeably longer than that for the Mg-Mg pair correlations.

The results in Figure 5.8 can be interpreted in terms of particle/matrix compositions and particle sizes if a model for the phases is proposed. Here, it has been assumed that the particles in the APT volumes are spherical, the radii of the particles following a log-normal size distribution. Analysis of the iso-contour data in Figure 5.7 suggests that the aspect ratio of the particles increases on aging from \( \sim 1 \) at 20 min to close to 2 at 160 min of aging. Nevertheless, the assumption of spherical particles has been retained, so as to keep the number of fitting parameters as small as possible. Moreover, the effect of this approximation on the prediction of yield strength based on particle size presented below, is expected to be nearly insensitive to this assumption for such small aspect ratios [27].

To account for the fact that the pair correlations in Figure 5.8 do not scale with one another, two populations of particles have been considered to exist, one being richer in Cu, with a larger correlation length compared to the other (see Appendix D, for details). From fitting \( \gamma_{Mg-Mg}(0) \), \( \gamma_{Cu-Cu}(0) \) and \( \gamma_{Cu-Mg}(0) \) it would be desirable to independently obtain the particle compositions and volume fractions (for the assumed two particle types), as well as the matrix composition. In order to do this, one extra piece of information needs to be supplied. In the present case it is assumed that the particles contained 80 at% Al, based on the profiles in Figure 5.7.

Under the above assumptions it was possible to obtain two size distributions and particle compositions

\(^3\)The origin of this expression can be consulted in Appendix C.
Figure 5.8: Experimental (symbols) and fit (coloured lines) pair correlation functions for a) Cu-Cu pairs, b) Mg-Mg pairs and c) Mg-Cu pairs from the APT datasets shown in Figure 5.7. If all particles belonged to the same population having a uniform composition, then the three figures should simply scale with one another.
Figure 5.9: Normalized pair correlation functions of Cu-Cu, Mg-Mg, and Cu-Mg pairs corresponding to the volume aged a) 20 minutes and b) 160 minutes. If all particles belonged to the same population having a uniform composition, then the three figures should simply scale with one another.

from the APT volumes (Figure 5.10). The resulting fits to the pair correlations are shown as solid, coloured, lines superimposed on the experimentally determined pair correlations (symbols) in Figure 5.8. The values obtained from the fit are also given in Table 5.1. Consistent with the composition profiles shown in Figure 5.7, the particles are seen to be systematically richer in Mg than Cu, with the Cu:Mg ratio being highest in the largest precipitates. With increased aging time, both distributions are seen to shift to larger particle sizes, again qualitatively consistent with the results from the isocomposition plots (Figure 5.7). Interestingly, the volume fractions of the two populations are observed to remain constant. This would also be consistent with the resistivity results (Figure 5.6) when interpreted using resistivity models [147, 148] that predict...
cluster contributions to the resistivity proportional to volume fraction, and provide also an explanation for the resistivity decrease at long aging times observed at 200°C, likely due to the coarsening of the particle distribution.

Figure 5.10: The best fit log-normal size distributions corresponding to the pair correlations shown in Figure 5.8. Left: aging for 20 min at 200°C. Right: aging for 160 min at 200°C. The green and red areas account for the respective amounts of Cu and Mg in the particles. The results are given as a volume weighted distribution, or $\frac{df_c}{dR}$.

<table>
<thead>
<tr>
<th>Aging Time</th>
<th>Particle</th>
<th>$\langle R \rangle$</th>
<th>$S$</th>
<th>$f_v$</th>
<th>$N_v$</th>
<th>Al (at%)</th>
<th>Cu (at%)</th>
<th>Mg (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>Cu Lean Particles</td>
<td>0.73 nm</td>
<td>0.48</td>
<td>0.23%</td>
<td>$4.9 \times 10^{23}$ m$^{-3}$</td>
<td>80</td>
<td>1</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Cu Rich Particles</td>
<td>2.2 nm</td>
<td>0.4</td>
<td>0.16%</td>
<td>$1.8 \times 10^{22}$ m$^{-3}$</td>
<td>80</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>160 min</td>
<td>Cu Lean Particles</td>
<td>2.4 nm</td>
<td>0.16</td>
<td>0.23%</td>
<td>$3.6 \times 10^{22}$ m$^{-3}$</td>
<td>80</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Cu Rich Particles</td>
<td>3.2 nm</td>
<td>0.4</td>
<td>0.17%</td>
<td>$6.3 \times 10^{21}$ m$^{-3}$</td>
<td>80</td>
<td>7</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 5.1: The mean particle size ($\langle R \rangle$) and standard deviation ($S$) of assumed log-normal particle size distribution, volume fraction ($f_v$), number density and composition of particles obtained by fitting to the data in Figure 5.8 assuming two log-normal particle size distributions in each aging condition. The Al content was fixed at 80 at% based on the composition profiles extracted in Figure 5.7.
5.2 Discussion

Mechanical Properties and Precipitation

If the features described in Figure 5.10 are responsible for the evolution in yield strength reported in Figure 5.5 it should be possible to use the data to predict the evolution of yield strength with time. Calculating the strength of such a distribution of precipitates must be done carefully as the way in which one chooses to calculate the average strength of such an assembly can have a strong influence on the prediction [26, 149]. Here, for simplicity, a modified approach to the one originally proposed by Deschamps et al. [111] has been taken, where the average strength of a distribution of obstacles is calculated as the average of the individual obstacle strengths [149]. It has been shown, by comparing to the results of areal glide simulations, that this approach provides a lower limit estimate to the strength of a distribution of obstacles, the predictions being better for narrower and weaker obstacle populations [26].

In a first instance, it is assumed that the strength of an individual particle is proportional to the radius of the circle (r) formed by the intersection of the spherical particle and the glide plane [150]. The distribution of circle radii (f(r)) formed by cutting the spherical particles (having a distribution of radii g(R), where R is the sphere radius) can be calculated from Wicksell’s fundamental integral equation [150, 151],

$$f(r) = \frac{r}{\bar{R}} \int_0^\infty \frac{g(R) dR}{\sqrt{R^2 - r^2}}$$ (5.7)

where $\bar{R}$ is the mean value of the sphere radii.

The contribution of the precipitates to the macroscopic yield stress is defined as,

$$\sigma_{ppt} = M \frac{G b}{\bar{L_s}} \bar{\tau}^*$$ (5.8)

where $M$ is the Taylor factor (M=3), $G$ is the shear modulus (G=26 GPa [152]) of aluminum and $b$ is the magnitude of the Burgers vector (b=0.29 [nm] [120]). The average square spacing of precipitates in the glide plane, $\bar{L_s}$, is taken following Ardell [20] as,

$$\bar{L_s} = \left( \frac{2\pi}{3f} \right)^{1/2} \bar{R}$$ (5.9)

The normalized average strength of the ensemble of particles, $\bar{\tau}^*$ is calculated as,

$$\bar{\tau}^* = \int_0^\infty \tau(r)^* f(r) dr$$ (5.10)

In this expression, $\bar{\tau}^*$ is the strength of a randomly distributed population of particles whose size in the glide plane is r. In the approach originally proposed by [111] the strength of obstacles was assumed to obey Friedel’s law, this only being strictly valid in the limit of weak obstacles. This approach was generalized by [149] to include obstacles of all strengths by using the classic result of Foreman and Makin [153] Here,
the same approach has been taken, but an updated relationship between obstacle strength and particle size arising from computer simulations, has been used[25],

\[
\tau (r) = \begin{cases} 
0.9 \left( \frac{r}{r_c} \right)^{3/2} \left( 1 - \frac{1}{6} \left( \frac{r}{r_c} \right)^5 \right) & \text{if } r < r_c \\
0.75 & \text{if } r \geq r_c 
\end{cases}
\] (5.11)

The parameter \( r_c \) in this expression is the critical size at which the particles transition from being shearable to non-shearable. It was noted, in relation to Figure 5.3 and 5.4, that the minor change in work hardening indicates the presence of shearable particles. When considering a distribution of particle sizes one must, however, consider the possibility of sizes that span a range of sizes from below to above \( r_c \).

The presence of two particle distributions (one lower in Cu, the other higher in Cu) leads to a question of whether one should use different \( r_c \) for each distribution. It has been argued, though not proved, that precipitation/cluster hardening in Al-Cu-Mg alloys is sensitive to the composition of the phases present [47]. Here, a single value of \( r_c \) has been chosen, so as to minimize the number of adjustable parameters. Even with a single value of \( r_c \), the two particle distributions (Figure 5.10) lead to two values of \( \sigma_{ppt} \) according to Equation 5.8. Considering that the strengths of these two particle distributions will be similar, the most appropriate method for their addition is by (see e.g. [154]).

\[
\sigma_{ppt} = \sqrt{\sigma_{ppt,1}^2 + \sigma_{ppt,2}^2} 
\] (5.12)

Finally, in order to calculate the total yield strength, the effect of solid solution contribution must be accounted for. From the particle compositions and volume fractions, we can calculate the remaining Cu and Mg in solid solution based on the bulk composition of the alloy. Assuming that the precipitated features have the same density as the matrix, the volume fraction of the precipitated features can be considered equal to the atomic fraction. As in the case of the precipitate contribution to the yield strength, the net contribution from the two solid solution alloys is expected to follow [26, 154].

\[
\sigma_{ss} = \sqrt{\sigma_{ss-Cu}^2 + \sigma_{ss-Mg}^2} 
\] (5.13)

where the solid solution hardening coefficients, \( k_{Cu} = 81.8 \text{ MPa/at.} \%^{2/3} \) and \( k_{Mg} = 27 \text{MPa/at.} \%^{2/3} \) are taken from [155].

Table 5.2 provides the various contributions from precipitates and solid solution to the overall yield strength. The relative average precipitate strength is also reported where \( \beta = F_m/2\Gamma \) where \( \Gamma \) is the dislocation line tension and \( \beta = 1 \) corresponds to the Orowan strength (\( r = r_c \)). To compute the total yield strength, the precipitate and solid solution contributions are summed as in Equation 5.13 and 5.12 owing to
their similar magnitudes. Finally, a constant term, $\sigma_0$, has been added to account for the effect of grain size,

$$\sigma_{ys} = \sigma_0 + (\sigma_{ss}^q + \sigma_{ppt}^q)^{1/q}$$  \hfill (5.14)

Where, assuming clusters and solute both represent weak obstacles, a value of $q = 2$ has been selected:

$$\sigma_{ss} = \sigma_0 + \sqrt{\sigma_{ss}^2 + \sigma_{ppt}^2}$$  \hfill (5.15)

The value of $\sigma_0$ was obtained directly by measuring the yield strength of a fully solution treated sample and subtracting the solid solution contribution calculated from Equation 5.13.

Using the above methodology with the particle size distributions from Figure 5.10 there remains only one unknown parameter ($r_c$) needed to calculate the yield stress. In order to fit the yield strength measured after 20 min of aging at 200°C (170 MPa), a value of $r_c = 3.95$ nm needs to be used. This is close to the equivalent value ($r_c = 5$ nm) used by Deschamps et al. to describe the precipitation hardening response of an Al-1.1at%Cu-1.7at%Mg alloy [46].

The selection of the $q$ exponent in Equation 5.14 can has been tested by calculating the dislocation releasing angle from the methodology described in [154]. A calculation of the average size resulting from the two particle size distributions results in a value of $q = 1.91$ for the sample aged 20 minutes, and $q = 1.66$ for the samples aged 160 minutes. These result closer to the used value of $q = 2$ which has been used to simplify the calculations.

<table>
<thead>
<tr>
<th>Aging Time at 200°C</th>
<th>$\sigma_0$ (MPa)</th>
<th>$\sigma_{ss}$ (MPa)</th>
<th>$\sigma_{ss}$ (MPa)</th>
<th>$r_c$ (nm)</th>
<th>$\beta\sigma_{ppt}$ (MPa) (Cu Rich)</th>
<th>$\beta\sigma_{ppt}$ (MPa) (Cu Lean)</th>
<th>$\beta\sigma_{ppt}$ (MPa) (Cu Lean)</th>
<th>$\sigma_{ys}$ (MPa)</th>
<th>$\sigma_{ys}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>20</td>
<td>30</td>
<td>58</td>
<td>3.95</td>
<td>104</td>
<td>87</td>
<td>0.2</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>160 min</td>
<td>20</td>
<td>29</td>
<td>58</td>
<td>3.95</td>
<td>104</td>
<td>87</td>
<td>0.2</td>
<td>195</td>
<td>196</td>
</tr>
</tbody>
</table>

**Table 5.2:** Parameters used/calculated in predicting the yield strength of the alloy after aging for 20 min and 160 min at 200°C. The relative strengths of the particles ($\beta = F_m/2\Gamma$) are also reported.

Having established a value for $r_c$ one can test the method’s ability to predict the yield stress after aging for 160 min, the results being shown in Table 5.2. One can see that the predicted value of the yield stress (195 MPa) is nearly identical to that measured experimentally (196 MPa). It is important to note that this good prediction would not have been possible if, in Equation 5.8 the mean radii of the distributions to calculate $\tau^*$ [149] had been used. Indeed, fitting the yield stress after 20 min of aging would require $r_c = 3.8$ nm leading to a predicted yield stress of 211 MPa in contrast to the experimental value of 196 MPa.

**Clustering in Al-Mg-Cu Alloy**

As seen in the Literature Review (Section 2), the qualitative similarity of the hardening response of the low Cu alloys studied here and more conventional 2XXX series alloys has been interpreted as evidence of similar microstructural evolution on aging. Comparison of the observations presented here to those from more conventional Al-Cu-Mg alloys [47, 63] suggests similarities and differences. In the APT observations re-
ported in [47] and [63], following aging similar to that used here, the dominant feature of the microstructure was reported as solute clusters. Such clusters were described as roughly spherical solute enriched regions containing on average 24 solute atoms [63]. Upon aging up to peak strength (80 hours at 170°C) three different features were found to dominate; solute clusters (up to 100 atoms in size, < 4 nm in diameter), rod-like GPB zones (< 4nm in diameter and 10-60 nm in length) and large plate like S-phase precipitates.

The features seen in Figure 5.7 and quantified via the pair correlation analysis in Figure 5.10 seem to situate somewhere between the features reported at short aging times and long aging times in the Al-Cu-Mg alloys noted above [47, 63]. The solute clusters reported in [63] after 30 min of aging at 170°C are similar in size and morphology to the average size of the Cu lean particles in Figure 5.10 after 20 min of aging. At the longer aging times, the size of the Cu rich particles along with the tendency for more rod-like morphologies suggests a transition towards more GPB like particles, according to their definition in [47].

A significant difference between the clusters/GPB zones reported in [63] and the particles observed here are the particle chemistries. While the cluster/GPB zones in [63] were found to have Mg:Cu ratios on the order of 1.1-1.3, here the Mg:Cu ratio was found to range from as high as 16 (in the Cu lean particles at 20 min of aging) to as low as 2 (in the Cu rich particles after 160 min of aging). What is consistent with regard to chemistry across both studies, however, is that in all cases the particles are predominantly made up of Al; ~ 80 at% in this study and between ~ 85 and ~ 90at% in [63]. The enrichment in Mg found here may not be entirely surprising considering the much higher bulk Mg:Cu ratio (14:1) for the alloy studied here compared to 0.97:1 in the alloy studied in [63]. This enrichment, combined with the high Al content of the particles, is a significant factor in the relatively high number density of particles ($N_v \approx 10^{23} \text{ m}^{-3}$) despite the low Cu levels employed. It is interesting to note that the behaviour seen here where small amounts of Cu can catalyze precipitation in Al-Mg alloys, qualitatively mirrors the behaviour seen in Al-Cu alloys where rapid hardening is only observed when small additions of Mg are made to the alloy [47]. Indeed, the precipitation strengthening observed here is quite comparable to that reported in more conventional Al-Cu-Mg alloys despite a lower number density of particles. For example, an Al-2.5wt%Cu-1.5wt%Mg alloy has been reported to harden by $\Delta \sigma \approx 80 \text{ MPa}$ after 100-200 min of aging at 200°C [46]. In the case of the 0.23at%Cu alloy studied here, $\Delta \sigma = 108 \text{ MPa}$ evaluated after 160 min of aging at the same temperature. The strengthening potential of these clusters/GPB zones may relate to a point made in relation to strengthening in Al-Cu-Mg alloys [47] where it was argued that particles richer in Mg seemed to be more effective at hardening compared to those rich in Cu.

The ability of even very small Cu additions to efficiently catalyze the formation of a relatively high number density of predominantly Al-Mg strengthening particles at short aging times is emphasized by the results obtained for the alloy containing only 0.12at%Cu (Figure 5.5). One can double the solutionized yield strength of both alloys studied here ($\Delta \sigma = 90 \text{ MPa}$ for 0.23at.%Cu and $\Delta \sigma = 67 \text{ MPa}$ for 0.12at.%Cu) by aging for 20 min at 200°C, this despite the fact that one alloy has half as much Cu as the other. These results support those originally reported in [6] where strengthening was achieved for alloys containing as little 0.08at%Cu. This is important given the aim of counterbalancing the ~ 25% loss in strength during the paint bake cycle [6] with the minimal addition of Cu.
Developing a Simplified Model for Aging Kinetics

The above sections provide a detailed overview of the complex microstructure and its relation to the age hardening response in the Al-Mg-Cu alloys studied here. It is clear that a parameter free method for predicting the aging response without direct measurement of the microstructure is not possible yet. It would still be valuable, however, to have a simplified method that can capture the experimentally observed trends observed in this work as well as in previous studies. Here, an approach is adopted that follows the spirit of classic process models (e.g. that of Shercliff and Ashby [156]) where the aim is to capture the correct response with a minimum number of fitting parameters and experimental evaluations.

It is notable that the yield strength varies linearly on a logarithmic time scale (Figure 5.5) for the alloys studied here. This behaviour has also been reported for similar alloys by Court and Lloyd [6], Ratchev et al. [133] and Kovarik et al. [8]. This does not obey the typical time evolution of yield strength in classical precipitation hardening systems where the precipitate size and volume fraction evolution are governed by nucleation and growth [88, 111].

Returning to the results of the APT observation, it was pointed out that the volume fraction of the clusters/GPB zones did not appear to evolve with time for the two times observed (within the linear yield strength-log(time) regime), though the average size of the features did increase. One possible interpretation of this, is that the growth of the clusters/GPB zones is governed by coarsening within this time/temperature domain.

Taking the simplest possible approach, let us assume that the average size of the clusters/GPB zones evolves following a simple coarsening law [156, 157]

\[
\bar{r}^3 - \bar{r}_0^3 = \frac{8\gamma D_mC_mC_{\beta}V_{\beta}}{9RT} t \tag{5.16}
\]

Where \(\bar{r}\) is the average cluster/GPB zone radius, \(\bar{r}_0\) is the initial radius, \(\gamma\) is the particle-matrix surface energy, \(D_m\) is the diffusivity of the solute, \(C_m\) the matrix concentration of solute, \(V_{\beta}\) the atomic volume of forming phase \(\beta\), \(R\) the gas constant and \(T\) the absolute temperature, and \(t\) is the time [157].

Next, to simplify the precipitation strengthening model used in the previous section two approximations will be made. First, it will be assumed that the strength arising from the precipitate distribution can be adequately captured by the average size of the distribution. While this assumption is at odds with the findings from the previous section (i.e. that knowledge of the full size distribution is important for predicting the strength accurately), this approach will allow us to write a closed form expression for the yield strength evolution with time involving a minimum of adjustable parameters. The second assumption is that rather than using the full form of equation 5.11 [26], it is assumed that the clusters/GPB zones are can be sheared by dislocations and that the simpler Friedel’s (Section 2.1) approximation can be used [20].

With these two approximations we can then write the strength arising from the clusters/GPB zones of
average size $\bar{r}$ and volume fraction $f_v$ as,

$$\sigma_{ppt} = M \left( \frac{3}{2\pi} \right)^{1/2} \frac{G_b}{r_c^{3/2}} f_v^{1/2} \bar{r}^{1/2}$$

(5.17)

where all of the terms have been previously defined in section (Section 2.1). Recall that all but one of the parameters in Equation 5.17 are material parameters or are constants (including $f_v$ due to the assumed coarsening response), the only parameter varying with aging time being the average size, $\bar{r}$.

Substituting $\bar{r}$ from Equation 5.16 into Equation 5.17 allows one to write the time evolution of the cluster/GPB zone contribution to the flow stress as [156]:

$$\sigma_{ppt} = A_0 t^{1/6}$$

(5.18)

with,

$$A_0 = M \left( \frac{3}{2\pi} \right)^{1/2} \frac{G_b}{r_c^{3/2}} f_v^{1/2} \left( \frac{8\gamma D_m C_m V^\beta}{9RT} \right)^{1/6} \frac{Pa}{s^{1/6}}$$

(5.19)

In what follows, $A_0$ is simply used as a fitting parameter, adjusted to fit the data from a given alloy aged at a given temperature.

For a given aging temperature and alloy content, one would expect that $\sigma_{ppt}$ should vary as approximately $t^{1/6}$ based on the above argument. Figure 5.11 shows the aging response of the two different Al-Mg-Cu alloys studied here for a variety of aging temperatures all plotted on a log-log graph. In this case the contribution of clusters/GPB zones to the yield stress was determined from the experimental data as $\sigma_{ppt} = ((\sigma_{y.s.} - \sigma_0)^2 - \sigma_{SS}^2)^{1/2}$, where the contribution to strength from the solid solution ($\sigma_{SS}$) is considered constant for all cases, based on the finding of the previous section (Section 5.2). When $\sigma_{ppt}$ for each aging experiment is normalized by $A_0$ (Table 5.3) one finds that the data collapses onto a single straight line having a slope of $1/6$, as one would expect from Equation 5.18.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$A_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Alloy/Aging temperature)</td>
<td>$[Pa s^{1/6}]$</td>
</tr>
<tr>
<td>0.23 at.% Cu - 200°C</td>
<td>$3.95 \times 10^7$</td>
</tr>
<tr>
<td>0.23 at.% Cu - 160°C</td>
<td>$3.88 \times 10^7$</td>
</tr>
<tr>
<td>0.23 at.% Cu - 100°C</td>
<td>$2.83 \times 10^7$</td>
</tr>
<tr>
<td>0.12 at.% Cu - 200°C</td>
<td>$2.69 \times 10^7$</td>
</tr>
</tbody>
</table>

Table 5.3: Obtained $A_0$ values used to collapse the data shown in Figure 5.11

In the fitting performed for the data in Figure 5.11 the parameter $A_0$ was treated as a simple adjustable parameter for each different aging temperature and alloy composition rather than attempting to calculate its value depending on the parameters in Equation 5.19, requiring more information, particularly the cluster/GPB zone volume fraction and its dependence on aging temperature. A evaluation of the expected order of magnitude can be done by using Equation 5.19 and the data obtained in the past section for the case of
Figure 5.11: Experimentally obtained log $\sigma_{ppt}$ vs log time representation, corresponding the aging temperatures and alloy compositions indicated in the figure. The dashed red line has a slope of 1/6, compatible with coarsening kinetics. The experimental values have been normalized by the obtained $A_0$ value for each condition.

material aged at 200 °C. Using diffusivity data from [158], and assuming an interfacial energy of the order of 0.3 [J/m] [111], a value of $A_0 = 2.9 \times 10^7 \frac{D_0}{\gamma_S}$ was obtained, this in the order of magnitude of the values obtained in Table 5.3.

Despite the large number of simplifications made in deriving Equation 5.18, the $t^{1/6}$ evolution law for $\sigma_{ppt}$ appears to give a good representation of the experimental results for conditions relevant to the industrial paint bake cycle. The approach fails for very short aging times/low aging temperature (where the cluster/GPB zone volume fraction is likely not constant) or long aging times/high temperatures where the transition towards the equilibrium $S$ phase is likely to occur and where the assumption of weak obstacles is less valid. The value of such a simplified aging law is that it can be used to predict the aging response with a minimum of experimental measurements. Thus, for other alloys or other aging temperatures, one only needs to determine the value of $A_0$ by means of a minimum of two tensile tests. From a practical point of view this approach should permit a rapid evaluation of the effect of alloy chemistry and isothermal aging conditions on the age hardening behaviour in an industrial setting. Moving further to the prediction of $A_0$
based on alloy chemistry and aging temperature would require a better understanding of the evolution of the volume fraction of clusters/GPB zones as a function of aging. This is a challenging proposition given the metastability of the clusters/GPB zones and the poor understanding of the chemistry/structure of these zones.

5.3 Summary

- Additions of as little as 0.12at.%Cu to a binary Al-Mg alloy can lead to significant precipitation hardening, the observed precipitates being similar in size and chemistry to clusters/GPB zones previously reported in more conventional 2XXX-series alloys and model Al-Cu-Mg alloys.

- Using data extracted directly from APT measurements, the size distribution of particles could be used to predict the yield strength after aging 160 min at 200°C following calibration of the shearable/non-shearable radius from data collected after 20 min of aging.

- While the strengthening particles share similar size and geometry to clusters/GPB zones in higher Cu/lower Mg alloys [63], the chemistry of the particles observed here were much leaner in Cu. This observation helps explain the relatively large number density of clusters/GPB zones despite the low bulk Cu content.

- A highly simplified model has been presented that should allow for a practical prediction of the aging response of the studied alloys. This simplified model, when calibrated by a minimum of two tensile tests performed for each alloy/aging temperature should allow for the yield strength evolution to be predicted for times/temperatures relevant to the industrial paint bake cycle.

- Given the appreciable strengthening observed in these low Cu alloys, precipitation hardening in alloys containing very low Cu contents should be able to readily compensate for recovery induced softening in the industrial paint bake cycle.
Chapter 6

The Effect of Pre-Deformation on the Microstructural Evolution in Al-Mg-Cu Alloys

The last chapter gave a detailed overview of the correlation between microstructure and yield strength in Al-Mg-Cu alloys, aged starting from the as-solutionized state. For the paint bake cycle, the more relevant situation is the aging response starting from a pre-deformed microstructure [18, 79, 80]. As noted in the literature review, our understanding of the role of pre-deformation on microstructural and mechanical property evolution is poor. In this chapter, the effect of deformation (following solution treatment) on aging will be discussed for the alloys studied in the previous chapter. This chapter will focus mainly on the microstructural evolution, a detailed discussion of the mechanical response being left for Chapter 5. Owing to the similarity of the two alloys studied in the last chapter, the 0.23at.%Cu containing alloy will be focused on in this chapter.

6.1 Methodology

A detailed description of the materials and processing path was given in Chapter 4, here only brief reminder is given with a focus on details specific to this chapter. The starting state for the materials studied in this Chapter is the same as that used in the last Chapter (cf. Chapter 4.2.2). The material was cold rolled, then solution treated, and recrystallized by annealing at 550°C for 10 minutes. Following this, samples were deformed in uniaxial tension at 77K to a specific pre-defined flow stress (44 or 174 MPa). Deformation at 77K does not represent industrial processing conditions but has been used to avoid effects of dynamic strain aging, simplifying the analysis of coupled precipitation and recovery. Table 6.1 shows the approximate plastic strain value corresponding to the mentioned applied pre-deformation.

The samples were then stored in liquid nitrogen until ready to be aged. Aging of the pre-deformed samples was conducted at 160°C or 200°C in a stirred oil bath. Samples were then taken from the gauge
Table 6.1: Selected levels of deformation in terms of increase in work hardening, for the study of deformation prior to precipitation.

<table>
<thead>
<tr>
<th>$\Delta \sigma$ [MPa]</th>
<th>$\varepsilon_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>2 %</td>
</tr>
<tr>
<td>174</td>
<td>10 %</td>
</tr>
</tbody>
</table>

section of these tested tensile samples for further characterization by DSC, electrical resistivity, atom probe tomography and electron microscopy.

6.2 Results

6.2.1 DSC, Electrical Resistivity and Microstructure Evolution on Aging

As noted in the literature review (cf. Section 2.4), prior studies on Al-Mg-Cu alloys [60] have relied on DSC measurements to show the changes in precipitation behaviour following aging of Al-Mg-Cu alloys. Figure 6.1 shows the evolution of the DSC thermograms for Al-3.23 at.% - 0.23 at.%Cu samples having been subjected to a variety of levels of deformation. As noted in Section 5.1.2 (Figure 5.2) Peak A has been previously associated to the formation of co-clusters/GPB zones [60, 132]. Here it is seen to broaden particularly towards higher temperatures, this effect increasing with the magnitude of pre-deformation. The endothermic peak B, which is associated with the dissolution of co-clusters/GPB zones [60, 132], is also broadened but still retained regardless of the level of deformation. Finally, Peak C associated with the formation of S-phase [60, 132], is seen to become sharper and shifted to lower temperatures with increasing pre-deformation. The broadening effect of the exothermic peak A has been observed by Ratchev et al. [60], using a similar system as the one studied here, uniaxially deformed 2 and 5% strain (their results are presented in Figure 2.17). In their interpretation, this broad exothermic signal is associated to the early formation of what they called S” phase along dislocations. The shift of the exothermic peak C, with further deformation, was also detected by Ratchev et al.[60]. Both effects support an earlier precipitation of S phase, assisted by the presence of dislocations.

In contrast to the rather significant changes observed in the DSC response as a function of pre-deformation, the changes in the electrical resistivity are much smaller. Figure 6.2 shows the evolution of the electrical resistivity of samples pre-strained to increase the flow stress by $\Delta \sigma = 44$ MPa, and $\Delta \sigma = 174$ MPa, then aged at 200°C. These are plotted alongside the results presented in Chapter 5 for samples aged directly following solution treatment. The first data point on the far left of this plot gives the resistivity of the as-solutionized samples, while the second set of data points present the resistivity following pre-deformation (without aging). The subsequent data points show the resistivity evolution on aging.

For the case of material pre-deformed $\Delta \sigma = 44$ MPa, the behaviour is nearly identically to the as-solutionized case. The only notable difference is an apparent earlier transition to lower resistivity at long times. In contrast, pre-deforming to $\Delta \sigma = 174$ MPa results in a significant resistivity jump following defor-
Figure 6.1: Differential scanning for Al-3.23 at.%Mg - 0.23 at.%Cu deformed to increase the flow stresses by $\Delta \sigma = 24$ MPa ($\varepsilon \approx 0.5\%$), 34 MPa ($\varepsilon \approx 1\%$), 44 MPa ($\varepsilon \approx 2\%$), 114 MPa ($\varepsilon \approx 8\%$) and 174 MPa ($\varepsilon \approx 10\%$). The curves have been offset vertically for easier visualization. A scanning rate of $5^\circ$ C/min. was used.

The jump in resistivity directly following deformation to $\Delta \sigma = 174$ MPa, raises the possibility that clustering occurred during the processing of the material despite the fact that the deformation was performed at 77 K and no artificial aging was conducted. It has, however, been previously shown that deformation in non-precipitation hardenable Al-Mg alloys can also lead to resistivity increases [159–161]. To test this, the AA5252 alloy was subjected to the same solution treatment, pre-deformation and aging schedule as the Al-Mg-Cu alloys. It is important to note that the material was pre-deformed to increment the flow stress by $\Delta \sigma = 174$ MPa, the same as in the case of the Al-Mg-Cu alloy. By choosing the same $\Delta \sigma$, the aim is to insure comparable dislocation density. Figure 6.3 shows the resistivity of the as-solutionized material, the...
Figure 6.2: Resistivity evolution of Al-3.23 at.% Mg - 0.23 at.%Cu alloy with pre-deformed $\Delta\sigma = 44$ MPa and $\Delta\sigma = 174$ MPa, aged at 200°C.

material after pre-deformation and after three aging times at 200°C.

The first important conclusion from this plot is that deformation can increase the electrical resistivity in the AA5252 alloy by an amount ($\Delta\rho \approx 0.6$ [nΩm]) nearly identical to that seen in the Al-Mg-Cu alloy ($\Delta\rho \approx 0.65$ [nΩm]). Thus, it is likely that the high resistivity following pre-deformation of the Al-Mg-Cu alloy is not due to deformation induced dynamic precipitation or to natural aging, rather it is a consequence of deformation induced defects [162]. The second important conclusion is that, upon aging, the resistivity drops rapidly back to the value of the as-solutionized material (within 2 minutes of aging). This helps to explain why all three curves (two different $\Delta\sigma$ and the as-solutionized case) show the same resistivity within the plateau ($t \lesssim 100$ min) in Figure 6.2.

6.2.2 Yield Stress Evolution on Aging

As seen in the last chapter (Chapter 5), the yield strength evolution in these alloys is also a sensitive macroscopic measure of the evolution of the microstructure during aging. In the case of pre-deformed samples, there is the additional complexity of separating the effects of softening by recovery, and hardening by precipitation as described in the literature review (section 2.5.2).

Figure 6.4 shows the yield strength evolution on aging at 200°C, for samples pre-deformed to increase the initial yield stress (before aging) by 44 and 174 MPa. As in Figure 6.2, these are plotted alongside
the aging response of the as-solutionized material. The first panel shows the yield strengths of the as-solutionized (blue) and pre-deformed (red and green) samples. For material pre-deformed by $\Delta \sigma = 44$ MPa, the magnitude of the rapid hardening effect is significantly lower than in material with no pre-deformation, measured from the as-deformed value (an increase of $\approx 34$ MPa vs. $\approx 65$ MPa is the non-deformed material).

In the case of material pre-deformed 174 MPa, a quick drop in yield stress ($\approx 32$ MPa) after the first 2 minutes of artificial aging can be observed. The yield stress evolution following this initial rapid change is, in all cases, seen to evolve with the same kinetics; the slopes of the linear portions of the yield stress vs log(time) curves being the same (consistent with $\sigma_{ppt} \propto t^{1/6}$).

The rapid decrease of yield strength in the alloy pre-deformed $\Delta \sigma = 174$ MPa is likely a consequence of recovery. This would be consistent with the discussion of the measured evolution of the electrical resistivity presented above. In that case it was argued that, for this state, the lack of a rapid increase in resistivity was a consequence of the counterbalancing effects of cluster/GPB zone formation and defect recovery in the first minute of aging.

Interpreting the results in Figure 6.4 is complicated by the fact that the yield strength in these alloys is a result of cluster/GPB zones ($\sigma_{ppt}$), solid solution ($\sigma_{ss}$), and forest dislocations ($\sigma_\perp$). In Chapter 7 a direct method to separate these contributions will be proposed. Here, a simpler approach will be adopted allowing for (at minimum) the identification of the sense of how pre-deformation can affect the cluster/GPB

**Figure 6.3:** Resistivity evolution corresponding to a AA5252 alloy containing 2.93 at.% Mg, deformed $\Delta \sigma = 174$ MPa, aged at 200°C.
Figure 6.4: Yield stress evolution of samples with no pre-deformation, and pre-deformed $\Delta \sigma = 44$ MPa and $\Delta \sigma = 174$ MPa, aged at 200 °C.

zone hardening relative to the solid solution state studied in Chapter 5.

One way to estimate an upper bound value for the rate of recovery in the Al-Mg-Cu alloy is to evaluate the recovery rate in a Al-Mg binary alloy containing the same Mg content and level of pre-deformation (i.e. the same dislocation density). Recovery in this Al-Mg alloy could be considered to provide an upper bound estimate for the rate of recovery in the Al-Mg-Cu alloy, under the assumption that the main effect of the Cu addition is to slow recovery by means of precipitation (cf. Section 2.5.2).

To evaluate the rate of recovery as described above, a set of experiments were performed on the AA5252 alloy (Approximately a binary Al-Mg alloy), mirroring the experiments presented above for the Al-Mg-Cu alloy. While the AA5252 alloy contains 0.3at%Mg less Mg than the Al-Mg-Cu alloy, such a minor difference in Mg has been shown to have a small effect on the rate of recovery for Al-Mg alloys (See the data for Al-3wt.% Mg from Barioz et al. reported in [32] vs. the data from Verdier et al. [37] for the case of Al-2.5wt.% Mg, tested under same processing and aging conditions). The AA5252 alloy was pre-strained in tension at 77K to increase the flow stress by 44 MPa and 174 MPa. These samples were then annealed for various times at 200 °C, the yield strength measured after annealing by performing tensile tests at 77K. The results of these tests are shown in Figure 6.5. It can be seen that the results shown in Figure 6.3 and Figure 6.5 are consistent in the sense that both resistivity and yield stress are seen to drop rapidly within the first minute of annealing. Moreover, beyond the first minute both resistivity and yield stress are seen
to remain approximately constant for times of up to 420 min. The yield stress evolution shown in 6.5, seems to be at odds with the classically observed linear reduction in a logarithmic time-scale (Section 2.2). Similar results have been reported by Verdier et al. [163] for material with low levels of pre-deformation, as in the experimental conditions used here. Furthermore, pre-deformation at 77K on high purity Al, has shown faster kinetics of recovery compared to samples deformed at room temperature [35, 164]. Despite the difference in kinetics of recovery, the magnitude of retained as-deformed flow stress, in the recovered state, is similar to the values reported after stabilization treatment in Al-2.4wt.%Mg alloy [32]. For the purposes of this discussion, it will be assumed that the yield strength of the AA5252 alloy is approximately constant for aging times of between 2 minutes and 420 minutes.

To take this one step further, an attempt can be made to provide an estimate of $\sigma_{ppt}$ from the data in Figures 6.4 and 6.5. Following the approach in [154], the general additivity law is defined as,

$$\sigma_{ys} = \sigma_0 + (\sigma_n^q + (\sigma_{ss}^q + \sigma_{ppt}^q)^n/q)^{1/n}$$

(6.1)

where $\sigma_0$ is the intrinsic and grain size contribution. Assuming no loss in solid solution, no contribution due to precipitation, and dislocations to be significantly stronger obstacles compared to solute, the selected exponent are $q = 2$ and $n = 1$\(^1\), allowing to calculate the retained forest strengthening from the data in Figure 6.5 as,

$$\sigma_\perp = \sigma_{ys} - \sigma_{ss} - \sigma_0$$

$$= \sigma_{ys} - \sigma_{rex}$$

(6.2)

where $\sigma_{rex}$ accounts for the solid solution, grain size and intrinsic strength, and it was taken as the yield strength of the fully recrystallized AA5252 alloy. $\sigma_{ys}$ is the yield stress plotted in Figure 6.5. The forest strengthening contribution was estimated as $\sigma_\perp = 41$ MPa for the sample pre-deformed to $\Delta \sigma = 44$ MPa and 106 MPa the sample pre-deformed to $\Delta \sigma = 174$ MPa. Now, if we assume $\sigma_\perp$ obtained in this way as an upper estimate to the degree of softening experienced by recovery in the Al-Mg-Cu alloy, then from Equation 6.1, we can estimate $\sigma_{ppt}$ as,

$$\sigma_{ppt} = \sqrt{(\sigma_{YS} - \sigma_0 - \sigma_\perp)^2 - \sigma_{ss}^2}$$

(6.3)

The same q and n exponents have been used, based on the findings in Section 5.2, where the strength of solute and clusters/GPB zones are considered similar and, as considered above, dislocation are considered stronger than the previous two, meaning that a Pythagorean addition law is appropriate. The value $\sigma_{ss}$ can be approximated as constant ($\sigma_{ss} = 65$ MPa), and, as previous Chapter (Chapter 5) a value of $\sigma_0 = 20$ MPa was used. Substituting the constant value of $\sigma_\perp$ obtained from the AA5252 alloy then allows for $\sigma_{ppt}$ to be estimated.

Figure 6.6 shows the values of $\sigma_{ppt}$ estimated in this way for the Al-Mg-Cu alloy pre-deformed to $\Delta \sigma$

\(^1\)Using the method in [154] indicates a value of $n = 1.13$, here simplified to $n = 1$. 

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Figure 6.5: Yield stress evolution corresponding to the AA5252 alloy, pre-deformed $\Delta\sigma = 44$ MPa, and $\Delta\sigma = 174$ MPa. Also plotted is the value of $\sigma_{ppt}$ obtained for the same alloy and aging temperature in Chapter 5. As we can see, the values of $\sigma_{ppt}$ for the pre-deformed samples found in this way both lie below that of the curve obtained for the material aged from the as-solutionized state. Recalling that $\sigma_\perp$ estimated from the AA5252 alloy should represent a lower bound estimate, means that the values of $\sigma_{ppt}$ for the pre-deformed samples should represent an upper bound estimate. The fact that these upper bound estimates still lie below the value of $\sigma_{ppt}$ for the solutionized sample suggests that the effect of pre-deformation is to reduce the number density of clusters/GPB zones. This interpretation also must consider the fact that the $\sigma_{ppt}$ vs log$t$ curves all well fit a $t^{1/6}$ evolution law, suggesting that beyond the first minute at 200°C the evolution of the clusters/GPB zones is very similar in all three cases. A detailed quantitative analysis of the previously observed change in mechanical response, will be given in Chapter 7.

Finally, while not shown here, the aging response of the pre-deformed materials was also evaluated at 160 °C. The results of these experiments are shown in Appendix E, the results showing the same trends as for those reported here.

6.2.3 Microstructural Observations

The results shown in Figure 6.6 suggest that for the same aging time at 200°C quite different microstructural states should exist, particularly with respect to the clusters/GPB zones. To evaluate this, samples of material
deformed $\Delta \sigma = 174$ MPa and aged at 200 °C for 20 and 160 minutes were selected for APT analysis. These match the times/temperatures analyzed by APT in Chapter 5.

Figure 6.7 show the reconstructed volume corresponding to Al-3.23 at.% - 0.23 at.%Cu alloy, deformed $\Delta \sigma = 174$ MPa, aged at 200 °C for 20 minutes. This reconstruction, accounting for a volume of 761484 nm$^3$, was analyzed by means of iso-concentration surfaces, and one dimension composition profiles. The observed features were defined using a surface with a Mg density of 3.2 atoms/nm$^3$. Comparing this volume to the one shown in Figure 5.7a, corresponding to the same aging time and temperature but without deformation, one sees significant differences. While one can still find some small roughly equiaxed features similar in size to those shown in Figure 5.7a (circled features), the most prominent features are most likely dislocation segments decorated by segregated solute, these indicated by the red lines on the figure, similar as the features reported in [165] as dislocation segments. Examining one-dimensional concentration profiles obtained in the perpendicular direction of these features (cf. profile shown in Figure 6.7), the profile shows peak concentrations of $\approx 12$ at. % Mg and $\approx 3.5$ at. % Cu along these volumes.

Figure 6.8 shows an APT volume extracted from the sample aged for 160 minutes, this reconstruction comprising an analyzed volume of 1851280 nm$^3$. Here, iso-concentration surfaces were plotted using a Mg density of 3.5 atoms/nm$^3$. This volume appears similar to the one shown in Figure 6.7 but very different from the one shown in Figure 5.7b, again the presence of non-equiaxed linear features dominates the volume,
though a few small isolated, roughly equiaxed features can also be found. Enrichment of solute along the linear features is confirmed by one dimensional chemical composition profiles (see examples shown in 6.8), with Mg enrichment as high as $\sim 20\%$ and Cu enrichment as high as $\sim 10\%$. The Mg and Cu compositions, however, vary widely along these features as illustrated by the very large differences in Mg and Cu profiles shown in the one-dimensional profiles.

The morphological and chemical complexity of the features seen in Figures 6.7 and 6.8 precludes the use of the radial distribution analysis from Section 5.1.5, as it requires the assumptions of a simple second phase shape and uniform composition. In this case a more detailed analysis using iso-surfaces and one-dimensional composition profiles across selected features was performed on the largest analyzed volume; one obtained from the sample aged for 160 minutes (Figure 6.8).

Focusing first on the small, isolated, equiaxed features observed at 20 minutes and 160 minutes (e.g. Figure 6.8, particles (i) to (iii)), it was found that they had compositions close to those of the features found in Figures 5.7a and 5.7b for the undeformed samples. This confirms that the clusters/GPB zones observed in the undeformed samples, and interpreted as being responsible for the hardening response, are present in the aged, pre-deformed samples. It would appear, however, that these clusters/GPB zones are present in much smaller densities in the pre-deformed samples compared to those found in the solutionized and aged samples. Of course, it is difficult to have good statistics from the limited APT observations reported here, but this observation, would correlate with the slower aging response in the pre-deformed samples (Figure

**Figure 6.7:** Analyzed APT reconstructed volume corresponding to Al-3.23 at.% - 0.23 at.%Cu alloy, deformed $\Delta \sigma = 174$ MPa, aged at 200 $^\circ$C for 20 minutes. The isosurface has been defined using a concentration of 3.2 atoms/nm$^3$ of Mg.
While it is impossible to identify dislocations in APT volumes, the linear features seen in the two volumes shown above, would appear to be consistent with segregation/precipitation on dislocations previously reported by other authors on similar systems using APT \[165, 166\]. It is notable that the maximum solute content regions found along these features exhibit a much higher solute concentration compared to the composition found for the equiaxed particles in Chapter 5. In the case of the sample aged for 160 min segments were found with compositions close to those expected for the S phase, i.e. Al$_2$MgCu (Figure 6.8, (iv)).

This preferential heterogeneous precipitation on dislocations was observed previously by Ratchev et al. [60] in Al-Mg-Cu alloys, by means of TEM. The phase that was observed was proposed as S" (Al$_2$CuMg), rather than S-phase directly. The observation of preferential precipitation of the S (or S-like) phase on dislocations would be consistent with two of the previous observations reported above. First, it was shown that increasing the level of pre-deformation shortened the plateau in the electrical resistivity (cf. Figure 6.3). The drop in resistivity in this case would be attributed to the rapid drop in solute in solid solution due to the removal of the much larger amounts of Mg and Cu required to form the S-phase compared to the low levels of Mg and (particularly) Cu required to form the clusters/GPB zones. The second observation consistent with the preferential formation of S-phase induced by the presence of dislocations is the shift to lower temperatures of the high temperature exotherm (Peak C in Figure 6.1) in DSC experiments, this peak having been associated with S-phase formation. Finally, some additional evidence for the preferential formation

\[ \Delta \sigma = 174 \text{ MPa}, \text{ aged at } 200 \, ^\circ\text{C for 160 minutes.} \]
of S-phase on dislocations has been obtained from observations of the microstructures after long aging at 200°C. Figure 6.9 shows a scanning transmission electron microscopy (STEM) image taken from within an SEM on a thin foil prepared from a sample deformed to 10% reduction by rolling at room temperature and then aged for 1100 min at 200°C. The retained (un-recovered) dislocation network is apparent in this case with rod-like precipitates decorating the dislocation network. The precipitates closely resemble (in size and shape) the S-phase precipitates identified by [60, 138].

![STEM image](image)

**Figure 6.9:** STEM in SEM observation of Al-3.23 at.% - 0.23 at.%Cu alloy, deformed by cold roll using a reduction of $\varepsilon = 10\%$, and aged at 200 °C for 1100 minutes. The retained dislocations appear to be decorated by precipitates, most likely S phase.

### 6.3 Rapid Hardening and the Role of Vacancies on Clustering/GPB Zone Formation

The key point from the results reported above is that pre-deformation leads to a reduction in the density of hardening clusters/GPB zones and an acceleration of the formation of equilibrium (or near equilibrium) S-phase by heterogeneous precipitation along dislocations. The effect of the pre-deformation on cluster/GPB zone formation appears to be most prominent, however, in the very earliest stages of aging (within the first minute of aging at 200°C). The main observation to be explained is the reduction in number density of clusters/GPB zones, in the case of the pre-deformed samples, and the fact that this appears to be dominated
by processes active during the very initial stages of aging, when the rapid hardening and rapid increase of resistivity are observed in the un-deformed samples.

Figure 6.10 provides a schematic view of the processes occurring during the aging of as-solutionized and as pre-deformed samples. In the as-quenched state the microstructure can be described as being composed of a random solid solution with a low density dislocations. The other important ingredient in the microstructure, essential for the formation of clusters in the early stages of aging, are quenched in (non-equilibrium) vacancies. As mentioned in Section 2.3 and 2.5.1, vacancies play a critical role in cluster/GP(B) zone formation by i) increasing the diffusivity of solute atoms [9, 17, 100, 101] and ii) by participating in the thermodynamic stabilization of small solute clusters[49, 70, 167]. Changes in vacancy concentration have been cited in a variety of aluminum alloys to explain unexpected changes in clustering behaviour depending on thermo-mechanical processing conditions [47, 111, 118, 119, 168].

Upon aging, the quenched in vacancies will allow for accelerated formation of clusters due to accelerated diffusion of solute, some of these vacancies becoming incorporated into the clusters/GPB zones. Those excess vacancies not captured within clusters/GPB zones may annihilate at other defects (dislocations and/or grain boundaries) or they may cluster to form dislocation loops [169]. Indeed, STEM observation on non-deformed and aged samples (starting from the as-solutionized state) show evidence of these processes in the form of helical dislocations and small dislocations loops in the Al-Mg-Cu alloys studied here (Figure 6.11). Similar observations have been made in Al-Cu-Mg alloys [138, 158]. The loss of these excess vacancies would be expected to i) slow the formation/growth of clusters/GPB zones due to the slower solute diffusivity and ii) reduce the nucleation of the clusters/GPB zones if vacancies are required for their stabilization. Thus, one explanation for the rapid initial hardening followed by the observed slow progressive coarsening observed in Chapter 5 would be the rapid decay of excess vacancies during aging.

In the case of the aging of pre-deformed samples a similar schematic picture can be envisioned. In this case however, deformation may modify the as-quenched excess vacancy concentration by the processes of deformation induced vacancy formation and annihilation. The rate of excess vacancy generation by low temperature plastic deformation has been modeled classically as, [105]

$$\frac{dC_{ex}}{dt} = \chi \frac{\Delta \sigma \Omega}{Q_f} \dot{\varepsilon}$$

Where $C_{ex}$ is the excess vacancy concentration, $\Delta \sigma$ is the increase in flow stress due to forest hardening, $\Omega$ the atomic volume, $Q_f$ the vacancy formation energy, $\dot{\varepsilon}$ the applied strain rate, and $\chi$ the vacancy production efficiency ($\chi \approx 0.1$[99, 101, 105]). This model has been previously applied to deformation generated vacancies in aluminum alloys [100, 101].

The annihilation of vacancies during deformation has also been previously considered [99] though for high temperature deformation where diffusion of vacancies to dislocations and/or vacancies has been con-

\footnote{Grain boundaries can also be an important microstructural feature but given the rather large grain size of the samples studied here, their effect on clustering/GPB zone formation will be ignored}

\footnote{At high homologous temperatures, a second generation term has been proposed due to the contribution of thermal jogs [99, 170]}
Figure 6.10: Schematic illustration of the microstructural processes envisioned to occur during aging. Top row: Aging starting from an as-solutionized state with a very low dislocation density Bottom row: Aging starting from a pre-deformed sample where significant vacancy annihilation can occur at forest dislocations.

sidered [99]. Given that the models for annihilation depend linearly on the self-diffusion coefficient, which is very small at 77K, the rate of annihilation for deformation at 77K is negligibly small relative to the rate of production predicted by Equation 6.4.

The production of vacancies and dislocations by plastic deformation should lead to an increase in electrical resistivity, these being the source of the increase in resistivity with pre-deformation shown in Figure 6.3. Figure 6.12 summarizes experiments performed on a number of samples of both the AA5252 alloy and the Al-3.23at%Mg-0.23at%Cu alloy where samples were pre-strained at 77K to different flow stresses. The electrical resistivity of these samples was then measured at 77K directly following deformation. The solid black line shows the predicted contribution to the electrical resistivity arising from the increasing dislocation density. The dislocation contribution to resistivity has been estimated from the measured increase in flow stress $\Delta \sigma_\perp$, via the Taylor equation,

$$ \Delta \sigma_\perp = M \alpha G \sqrt{\bar{\rho}} $$  \hspace{1cm} (6.5)

where $M$ is the Taylor factor ($M=3$), $\alpha$ represents the average strength of the forest dislocations ($\alpha=0.3$), $G$
is the shear modulus \((G=26 \text{ GPa} [152])\) of aluminum, \(b\) is the magnitude of the Burgers vector \((b=0.29 \text{ nm} [120])\), and \(\rho\) the dislocation density.

Solving Equation 6.5 for the dislocation density \(\rho\), and multiplying for the resistivity coefficient, \(K_{\perp}\),

\[
\rho_{\perp} = K_{\perp} \left( \frac{\Delta \sigma}{M \alpha G b} \right)^2
\]  

(6.6)

The resistivity coefficient, \(K_{\perp}\), for dislocations was taken as \(4 \times 10^{-16} \Omega \text{m}^4\) following previous work [171, 172]. One can see that this prediction underestimates the measured change in resistivity, suggesting that the remaining increase in resistivity could be due to the presence of deformation induced excess vacancies.

To test this, Equation 6.4 was used to predict the increase in excess vacancy concentration due to deformation, the values and sources of the various parameters given in Table 6.2. The contribution of these vacancies to the resistivity was then obtained as,

\[
\rho_{\text{vac}} = K_{\text{vac}} C_{\text{vac}}
\]  

(6.7)

where the scattering coefficient \(K_{\text{vac}} = 25 \Omega \text{m/\%}\) was taken from [171, 172]. Assuming Matthiessen’s rule [134], the observed increase in resistivity can be taken as the sum of the contributions from dislocation and vacancies, this being shown as the red line in Figure 6.12. It can be seen that the sum of these two contributions matches well with the experimental results up to a flow stress of \(\approx 250 \text{ MPa}\).
Figure 6.12: Resistivity contribution of vacancy and dislocation storage during deformation, compared to experimentally obtained resistivity measurements from Al-3.23 at.%Mg - 0.23 at.%Cu and AA5252 alloy

The most important conclusion from this result is that the vacancy concentration is not drastically changed relative to that expected in the as-quenched material. The equilibrium vacancy site fraction at the solutionizing temperature (550°C) was estimated as $0.7 \times 10^{-4}$ using the parameters in [14, 173]. Based on Equation 6.4, increasing the flow stress by $\Delta \sigma = 44$ MPa would only lead to a small increase (by $6 \times 10^{-6}$). Increasing the pre-deformation to $\Delta \sigma = 174$ MPa would lead to an increase of vacancy site fraction to $1 \times 10^{-4}$.

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<th>Value</th>
<th>Meaning</th>
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<td>$\Delta \sigma$</td>
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<td>Increase in flow stress by work hardening</td>
<td>Obtained from experiments</td>
</tr>
<tr>
<td>$\dot{\varepsilon}$</td>
<td>$7.3 \times 10^{-4}$ s$^{-1}$</td>
<td>Imposed Strain rate</td>
<td>Fixed experimentally</td>
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<tr>
<td>$\chi$</td>
<td>0.1</td>
<td>Vacancy production efficiency</td>
<td>[101, 105]</td>
</tr>
<tr>
<td>$Q_f$</td>
<td>0.67 eV</td>
<td>Vacancy formation Energy</td>
<td>[174]</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>$1.66 \times 10^{-29}$ m$^3$</td>
<td>Atomic volume</td>
<td>[101]</td>
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Table 6.2: Numerical values and their origin used in Equation 6.4 to predict vacancy formation during plastic deformation.

The second main difference between the aging of the as-solutionized and the pre-deformed samples is that a much higher density of sinks, i.e. dislocations, exists for vacancy annihilation in the pre-deformed sample compared to the as-solutionized sample. This is important as during aging there will be a competi-
tion between vacancy annihilation and vacancy incorporation into clusters/GPB zones. The recent work of Fischer et al. [109] has shown the importance of dislocation density on the rate of vacancy annihilation. In their model, the rate of annihilation can be written as,

$$\frac{dX_v}{dt} = -2 \left( \frac{2\pi \rho}{h_p f} \right) D_v \frac{X_v}{X_{v,eq}} \ln \left( \frac{X_v}{X_{v,eq}} \right)$$

(6.8)

where $X_v$ is the instantaneous vacancy site fraction, $X_{v,eq}$ is the (temperature dependent) equilibrium vacancy site fraction, $D_v$ is the diffusivity, $h_p$ is the density of jogs on dislocations, $\rho$ is the dislocation density and $f$ is a constant (of order 1). One can numerically solve Equation 6.8 to predict the time evolution the vacancy site fraction during quenching from the solutionizing temperature and/or to predict the vacancy site fraction evolution during aging. As shown in [109], for quench rates consistent with those used here (cf. Section 4) and for a dislocation density of $10^{10} - 10^{11} \text{ m}^{-2}$ the as-quenched vacancy concentration is retained to within a factor of $\sim 2$ of the equilibrium vacancy concentration at the solutionizing temperature (550°C).

More interesting is to examine the effect of the dislocation density on the rate of dislocation annihilation during aging. Figure 6.13 shows the time evolution of the vacancy site fraction obtained from Equation 6.8, parameterized using the data in Table 6.3. In this case it has been assumed that the material was heated from room temperature to 200°C at 100°C/s then held isothermally, this being consistent with the experiments (cf. Section 4). In the case of the conditions corresponding to $\rho = 10^{10} - 10^{13} \text{ m}^{-2}$, the initial vacancy concentration was taken to be the equilibrium concentration at the solutionizing temperature. In the case of the condition having $\rho = 10^{14} \text{ m}^{-2}$ the vacancy site fraction was increased by $1 \times 10^{-4}$, this being taken from the increased vacancy concentration estimated following plastic deformation to $\Delta \sigma = 174 \text{ MPa}$ by resistivity. Indeed, the conditions corresponding to $\rho = 10^{13} \text{ m}^{-2}$ and $\rho = 10^{14} \text{ m}^{-2}$ resemble the conditions expected for $\Delta \sigma = 44 \text{ MPa}$ and $\Delta \sigma = 174 \text{ MPa}$. 

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<td>Pre-exponential for diffusivity</td>
<td>[174]</td>
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<td>$Q_v$</td>
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<td>Activation Energy for Self-Diffusion</td>
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<td>$Q_f$</td>
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<td>Vacancy formation Energy</td>
<td>[109]</td>
</tr>
<tr>
<td>$h_p$</td>
<td>100</td>
<td>Jog density (per unit length)</td>
<td>[109]</td>
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<tr>
<td>$f$</td>
<td>0.7815</td>
<td>Geometric Factor for FCC crystals</td>
<td>[109]</td>
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Table 6.3: Numerical values used to predict vacancy annihilation during aging in Equation 6.8.

The key take-away from Figure 6.13 is that the excess quenched-in vacancies available in the as-solutionized condition, these samples having expected $\rho \approx 10^{10} - 10^{11} \text{ m}^{-2}$, will retain a large fraction of their excess vacancy concentration within the first minutes of aging. In contrast, the pre-deformed samples containing $\rho \approx 10^{13} \text{ m}^{-2}$ ($\Delta \sigma = 44 \text{ MPa}$) and $\rho \approx 10^{14} \text{ m}^{-2}$ ($\Delta \sigma = 174 \text{ MPa}$) will lose their excess vacancies within the first few seconds of aging. The sample with $\rho \approx 10^{14} \text{ m}^{-2}$ is even predicted to achieve...
Figure 6.13: A prediction of vacancy loss during aging in materials containing different dislocation densities ($\rho$). In all cases the samples were modelled assuming a heating rate of 100$^\circ$C/s from 25$^\circ$C to 200$^\circ$C. In the cases where $\rho = 10^{10}$-10$^{12}$ m$^{-2}$ the initial dislocation density was taken to be the equilibrium vacancy concentration at 550$^\circ$C. In the case of the samples with $\rho = 10^{13}$ and 10$^{14}$ m$^{-2}$ an additional excess vacancy concentration was added corresponding to that arising from plastic deformation.

the equilibrium fraction of vacancies prior to reaching 200$^\circ$C.

The analysis shown in Figure 6.13 does not incorporate information on two key factors. First, it does not include information on vacancy-cluster/GPB zone interaction. It is expected that if vacancies do play an important role in cluster/GPB zone formation there will be a competition between vacancy trapping in solute clusters and vacancy annihilation at dislocations. This will likely modify the kinetics from those shown in Figure 6.13. Qualitatively, however, this picture remains consistent with the aging response shown in Figure 6.6. In this picture, a larger number density of small solute clusters can be formed in the early stages of aging of the as-solutionized samples owing to the higher density of vacancies that can contribute to cluster/GPB zone formation in the first minutes of aging. In the case of the pre-deformed samples, a nearly equal reduction in cluster/GPB zone formation occurs in the early stages of deformation owing to a much larger fraction of vacancies being lost to annihilation on dislocations before they can participate in cluster/GPB zone formation.

A potentially more significant factor missing from the analysis in Figure 6.13 is the fact that the dis-
location density (in pre-deformed samples) is reduced by the process of recovery during aging. Using the recovery observed in the AA5252 alloy as a measure of the level of recovery observed in the Al-Mg-Cu alloy (cf. Figure 6.5) we see that the sample pre-deformed to $\Delta \sigma = 44$ MPa, retains a large portion of its work hardening (41 MPa out of 44 MPa) even after holding for $> 100$ minutes at 200°C. Using the Taylor equation the retained forest dislocation density can be estimated as $\rho = 3 \times 10^{13} \text{ m}^{-2}$. In the case of the sample pre-deformed by $\Delta \sigma = 174$ MPa, softening occurs to $\Delta \sigma \approx 106$ MPa, this corresponding to a retained dislocation density of $\rho = 2 \times 10^{14} \text{ m}^{-2}$. Thus, although the dislocation density does change due to recovery, the magnitude of dislocations is expected to remain in the $10^{13}-10^{14} \text{ m}^{-2}$ range for the duration of aging times of interest here at 200°C meaning that very fast annihilation of vacancies should be expected.

To this point the possible effects of solute segregation (and precipitation) to dislocations may effect the processes discussed above. As was shown in Chapter 5, cluster/GPB zone formation occurred with very little change in the overall composition of the matrix. Despite the significant amount of segregation/precipitation on dislocations revealed by Figure 6.7 (sample aged for 20 min) it was found that the matrix composition away from these features had not changed significantly. This may be partially attributable to the fact that the degree of segregation ($\sim 20\%\text{Mg,} < 10\%\text{Cu}$) remained relatively small. This is also consistent with the fact that the resistivity remained relatively constant during aging for times much longer than 20 minutes, suggesting that the solid solution contribution to the resistivity was not dropping drastically. At the longer time examined (Figure 6.8, 160 minutes) much more significant enrichment in Mg and (particularly) Cu was observed, with compositions approaching those of the S-phase being observed. The larger loss of solute from solid solution at these longer aging times would help to explain the drop in resistivity observed at long aging times. The important point, is that no significant change in matrix composition is expected within the first minutes of aging where the main effects of pre-deformation are observed on the aging response. Thus, depletion of solute by segregation to dislocations is unlikely to explain the changes in aging response observed between the as-solutionized and pre-deformed conditions.

If the above explanation for the effect of pre-deformation on aging response is correct, one might expect to find evidence for similar changes in the aging response of Al-Mg-Cu alloys depending on the vacancy concentration at the start of aging. One simple way to change the initial vacancy concentration without pre-deformation would be to change the quench rate and/or the solutionizing temperature. Kovarik et al.[8], noted a slightly higher yield strength for a Al-3wt.\%Mg-0.98wt.\%Cu solutionized at 550°C then quenched and aged compared to the same alloy solution treated at 510°C then quenched. This was despite the material having the same yield strength in the as-quenched state. It is also interesting to compare the results obtained in this work with those obtained by Court and Lloyd [6] on a very similar alloy. In [6] samples were allowed to air cool from the solution treatment temperature, this potentially resulting in a larger loss in excess vacancy concentration compared to the quenched samples studied here. After aging for 30 minutes at 200°C Court and Lloyd reported hardening of 66 MPa, compared to 105 MPa measured on the samples studied here. It is hard to be confident, however, that this difference has arisen from differences in quench rate alone. Preparation of the initial alloy, small variations in alloy composition and effects arising from storage of samples between solution treatment and aging could all have major effects on the aging response.
Finally, it is useful to reflect on the potential impact of these results on industrial processing conditions. The experimental procedure (low temperature deformation and storage of samples after deformation) chosen in this study represent conditions that will lead to promote excess vacancy retention during the early stages of deformation. In conventional processing performed at room temperature on material that may be solutionized and slowly cooled and held for significant periods of time at room temperature, lower excess vacancy concentrations may be expected. This will even out differences in the vacancy concentrations following deformation, leading to less of an effect of pre-deformation on the aging response.

6.4 Summary

The key observations and conclusions from this Chapter can be summarized as follows

- Deformation negatively affects the early stages of formation of clusters/GPB zones. Evidence for this comes from yield strength measurements, electrical resistivity and DSC observations.

- Recovery is not entirely suppressed by clustering/GPB zone formation. Rapid recovery occurs within the first seconds of aging at 200°C.

- APT observations reveal significant solute segregation on dislocations. An irregular pattern of segregation is observed after 20 minutes of aging, with local regions reaching compositions near those required for S-phase formation. This matches prior work that indirectly suggested rapid formation of the S-phase on dislocations.

- Despite this segregation, small clusters/GPB zones appear to still be present in the microstructure.

- It has been argued that rapid excess vacancy annihilation at dislocations is responsible for the reduction in cluster/GPB zone formation in the pre-deformed samples. This suggests that care must be taken to control the thermo-mechanical processing of samples to ensure reproducible aging response. That being said, the test conditions used here should be expected to give the largest contrast in the as-solutionized and pre-deformed behaviours.

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Chapter 7

Separating the Effects of Cluster Hardening and Recovery on the Aging Response of Al-3.23 at.% - 0.23 at.% Cu: Work Hardening Analysis

The last Chapter focused on assessing the microstructural changes arising from aging when starting from a pre-deformed state. One of the most significant challenges in that analysis was to unambiguously separate the effects of cluster/GPB zone hardening from recovery induced softening during aging. A simplified approach was presented using the recovery rate of the AA5252 alloy as a proxy for the recovery rate in the Al-3.23 at.% - 0.23 at.%Cu alloy. In this Chapter, a method for separating the effects of precipitation and recovery is proposed based on a combined analysis of yield strength and work hardening rate. This method provides a method for predicting not only the yield strength but also the overall stress-strain response following aging.

The method presented here is based on observations presented in the Chapter 5. There it was shown that most of the aging conditions used in this thesis lead to a form of precipitation hardening that increases the yield strength without changing the work hardening rate. Recovery, the reduction of dislocation density that occurs on aging (as shown in Chapter 6) leads to both a change in yield strength and a change in work hardening rate. Thus, a simple approach to separate the effects of recovery softening and cluster/GPB zone hardening should able to predict both yield strength and work hardening rate from the stress-strain response following aging of pre-deformed samples.

This chapter starts by presenting a more detailed analysis of the stress-strain response of the Al-3.23 at.% - 0.23 at.%Cu alloy aged at 160°C and 200°C following deformation. A particular focus is made on the work hardening response and its comparison to classic models. Following this, a model is developed that attempts to account for changes in yield stress and work hardening rate linked to the microstructural changes
described in Chapter 6. Finally, this method is used to separate the contributions of cluster/GPB zone hardening and dislocation based recovery softening, the results being discussed in relation to the conclusions reached in Chapter 6.

### 7.1 Experimental Results: Work Hardening Response Following Aging

The results presented in this Chapter come from many of the same samples discussed in Chapter 6, with additional results presented for samples aged at 160°C as well as for samples taken from the AA5252 alloy. As throughout the rest of this thesis, the tensile tests were all performed at 77K following the procedure outlined in Chapter 4. Similarly, details on the method used to age the samples can be found in Chapter 4.

Figure 7.1 shows the stress-strain response for all of the Al - 3.23 at.% - 0.23 at.%Cu alloy conditions studied in this Chapter. The solid black lines in each plot indicate the stress-strain curves of the as-solutionized material. The coloured lines show the stress-strain response of samples that had been pre-deformed to $\Delta \sigma = 44$ MPa (Figures 7.1a and 7.1b) or $\Delta \sigma = 174$ MPa (Figures 7.1c and 7.1d). In the case of the pre-deformed and aged samples, the stress-strain curves have been plotted starting from the level of pre-strain so as to illustrate the changes in the stress-strain response.

Focusing on the samples with $\Delta \sigma = 44$ MPa (Figures 7.1a and 7.1b) one can see that aging, even for 2 minutes, leads to the stress-strain curve jumps above the stress-strain curve of the as-solution treated material, the overall shape of the stress-strain curves all appearing similar. A more drastic effect of aging is seen for the samples with $\Delta \sigma = 174$ MPa (Figures 7.1c and 7.1d). In this case, aging leads to a drop in the flow stress for all but the longest aging times. However, on straining one can see that the work hardening rate (slope of the stress-strain curves) is higher for the aged material leading to the stress-strain curves of the aged samples crossing over the stress-strain curve of the as-solution treated samples (black curve). The insets in Figure 7.1 focus on the initial yielding behaviour where it can be seen that, aside from the change in yield stress, all aged samples exhibit a similar low work-hardening rate 'plateau' just following yielding.

A better way to visualize the evolution of the work hardening behaviour on aging is to re-plot the stress-strain curve as a Kocks-Mecking plot, i.e. to plot the work hardening rate ($\theta = d\sigma / d\varepsilon$) versus the flow stress [175]. Figure 7.2 shows the Kocks-Mecking plots for all of the stress-strain curves in Figure 7.1.

In all cases the blue curve shows the work hardening response of the as-solution treated sample. The low work-hardening regime observed for the aged samples in Figure 7.1 is revealed in the work hardening plots as a transient at the beginning of each of the work hardening curves. Focusing on the samples pre-deformed to $\Delta \sigma = 44$ MPa (Figures 7.2a and 7.2b) one sees that the work hardening (beyond the initial transient) looks similar to those presented in Figure 5.4 in Chapter 5, the work hardening plots being shifted in stress but similar in slope to the work hardening plot for the as-solution treated material. For samples pre-deformed to $\Delta \sigma = 174$ MPa the similarity between the work hardening behaviour of the aged and as-solution treated material becomes less clear.

Owing to the large number of conditions shown in Figure 7.2, it is difficult to see some of the significant but subtle differences in the work hardening rates. Figure 7.3 shows only the Kocks-Mecking plots for the
Figure 7.1: Stress vs. strain evolution of Al-3.23 at.% - 0.23 at.%Cu alloy, deformed a) and b) $\Delta \sigma=44$ MPa ($\epsilon_p=2\%$), during artificial aging at 160 and 200 °C respectively, and deformed c) and d) $\Delta \sigma=174$ MPa ($\epsilon_p=10\%$), during artificial aging at 160 and 200 °C respectively. All tensile tests were done at 77K.

as-solutionized state (blue curve) and for the materials aged for 2 minutes. These plots show that the Kocks-Mecking plots for the as-solutionized and lightly deformed material ($\Delta \sigma=44$ MPa) are well approximated as straight lines, consistent with the classic Kocks-Mecking analysis [175], having practically the same slope. On the other hand, the work hardening behaviour on samples pre-deformed $\Delta \sigma=174$ MPa, after 2 minutes of aging, shows an immediate change in the slope of the work hardening evolution. Comparing these plots to the Kocks-Mecking plots shown in Figure 5.4 in Chapter 5 shows significant differences between the work hardening behaviour following aging of pre-deformed samples compared to the work hardening behaviour following aging of the as-solution treated samples.
Figure 7.2: Kocks-Mecking plots resulting from the stress vs. strain data for Al-3.23 at.% - 0.23 at.%Cu alloy pre-deformed to $\Delta \sigma = 44$ MPa (a and b) and $\Delta \sigma = 174$ MPa (c and d). The plots on the left (a and c) show the response on aging at 160 °C while the plots on the right (b and d) show the response upon aging at 200°C. All tensile tests were done at 77K.

In Chapter 5 it was argued that for the majority of aging temperatures aging did not fundamentally change the work hardening behaviour. The differences observed here must come from differences in microstructure on aging of the pre-deformed reported in Chapter 6, e.g. changes in precipitation, segregation and precipitation on dislocations and/or dislocation recovery. To help test whether these effects are due primarily to changes in clustering/GPB zone formation in the aged samples, the work hardening behaviour of the AA5252 has been analyzed following the same pre-deformation and aging treatments used for the samples shown in Figures 7.1 and 7.3. Figure 7.4 shows the stress-strain response of the AA5252 alloy in the solution treated state as well as after pre-deformation to $\Delta \sigma = 44$ MPa and 174 MPa and aged at 160°C and 200°C. Figure 7.5 shows the Kocks-Mecking plots produced from the data in Figure 7.4.

It can be immediately seen that the AA5252 alloy, which is non-precipitation hardenable, shows the same
Figure 7.3: Kocks-Mecking plots resulting from the stress vs. strain data for Al-3.23 at.% - 0.23 at.%Cu alloy deformed a) and b) $\Delta \sigma = 44$ MPa, during artificial aging at 160 and 200 °C respectively, and deformed c) and d) $\Delta \sigma = 174$ MPa, during artificial aging at 160 and 200 °C respectively. All tensile tests were done at 77K.

features following pre-deformation and aging as the Al-Mg-Cu alloy, notably, the low initial work hardening behaviour followed by a evolution of the work hardening rate over the rest of the tensile test. These plots also show how, even for the lower level of pre-deformation, there is an increase in the non-linearity of the work hardening behaviour following yielding. These results suggest that it is not the process of clustering/GPB zone formation in the early stages of aging that leads to these changes in the work hardening response, rather it would appear that these changes are due to effects related to aging following pre-deformation in Al-Mg alloys.
Figure 7.4: Stress vs. strain evolution for AA5252 alloy (Al-2.94 at.% Mg) pre-strained a) and b) $\Delta \sigma=44$ MPa ($\varepsilon_p=2\%$), during artificial aging at 160 and 200 °C respectively, and deformed c) and d) $\Delta \sigma=174$ MPa ($\varepsilon_p=10\%$), during artificial aging at 160 and 200 °C respectively. All tensile tests were done at 77K.
Figure 7.5: Kocks-Mecking plots resulting from the stress vs. strain data for AA5252 alloy (Al-2.94 at.% Mg) pre-strained a) and b) $\Delta \sigma = 44$ MPa, during artificial aging at 160 and 200 °C respectively, and pre-strained c) and d) $\Delta \sigma = 174$ MPa, during artificial aging at 160 and 200 °C respectively. All tensile tests were done at 77K.

7.2 A Model for the Work Hardening Response of Pre-Deformed and Aged Samples

At the beginning of this chapter it was proposed to analyze the work hardening response of the Al-Mg-Cu samples to separate the effects of cluster/GPB zone hardening from recovery induced softening. The basic idea proposed was that cluster/GPB zone hardening (as shown in Chapter 5), leads to an increase in yield strength but no change in work hardening. Recovery due to the loss of dislocations, on the other hand, should lead to both a change in yield strength and work hardening rate. Here, an attempt to perform this separation will be taken where it is assumed that cluster/GPB zone hardening does not influence the work hardening rate, and that the effect of recovery can be captured by means of a modified Kocks-Mecking analysis.
The work hardening behaviour of single phase aluminum alloys has been shown to obey the classic Kocks-Mecking model for dislocation based work hardening [176, 177]. In this model, a single internal state variable (the dislocation density, \( \rho \)) is used to predict the dislocation evolution of the dislocation density and flow stress during plastic deformation,

\[
\frac{d\rho}{d\varepsilon_p} = k_1 \sqrt{\rho} - k_2 \rho \tag{7.1}
\]

Here, the first term is related to the storage of dislocations with progressive deformation. This storage term is proportional to the mean distance between dislocations, while the term \( k_1 \) account for the efficiency of such dislocation generation [175, 178]. The second term accounts for the rate of annihilation of dislocations by dynamic recovery. Dynamic recovery is assumed in the Kocks-Mecking model to be proportional to the dislocation density. The proportionality factor \( k_2 \) is sensitive to the deformation temperature, strain rate, and alloy composition [175, 177]. The stress required to move dislocations through a fixed dislocation density, the so-called “forest” strength, is given by the Taylor equation,

\[
\sigma_\perp = M \alpha G b \sqrt{\rho} \tag{7.2}
\]

Where \( \alpha \) represents the average strength of the forest dislocations (0.3 – 0.5), \( G \) the shear modulus, \( b \) the magnitude of the burgers vector, and \( \rho \) the dislocation density (line length per unit volume).

Combining the Equation 7.2 with Equation 7.1, allows the work hardening response in terms of the flow stress as,

\[
\theta = \frac{d\sigma_\perp}{d\varepsilon_p} = \theta_0 (1 - \frac{\sigma_\perp}{\sigma_v}) \tag{7.3}
\]

Where

\[
\theta_0 = \frac{\alpha G b M k_1}{2} \tag{7.4}
\]

\[
\sigma_v = \frac{\alpha G b M k_1}{k_2} \tag{7.5}
\]

It can be seen that Equation 7.3 predicts a linear decrease in the work hardening rate from \( \theta_0 \) at the onset of plastic deformation to zero at a ‘saturation stress’, \( \sigma_v \). The work hardening behaviour of the as-solution treated Al-3.23 at.% Mg - 0.23 at.%Cu and AA5252 alloy (Al-2.93 at.% Mg) are well represented by this model, the good fit being shown in Figure 7.6. The Al-3.23 at.% Mg - 0.23 at.%Cu alloy fit was obtained with a \( K_1=6.55x10^8 \) [1/m] and \( K_2=9.97 \) values, while AA5252 (Al-2.93 at.% Mg) alloy fit was obtained with a \( K_1=5.64x10^8 \) [1/m] and \( K_2=9.41 \) values.

A critical consequence of having a description of the evolution of the work hardening rate of the material,

---

1In reality the work hardening does not go to zero at \( \sigma_v \), rather it enters into a stage of deformation with a small but nearly constant rate of hardening often referred to as ‘Stage IV’ hardening [175]

2The difference in the measured \( K_1 \) values is coherent with previously reported increase in initial work hardening rate \( \theta_0 \) proportional to the Mg content in Al-Mg alloys [152]
during deformation, is that in principle all states of work hardening during plastic deformation are known and represented by Equation 7.3 (blue line Figure 7.7). If the same material has been pre-deformed by plastic deformation to a certain flow stress, corresponding work hardening rate (green square, Figure 7.7), and then subjected to a process that reduces the dislocation density and, thus, flow stress (e.g. static recovery), the result will be a correspondingly higher work hardening rate (red square, Fig. 7.7) as described by Equation 7.3. Re-loading the material, to continue deformation following this recovery process, should lead to the deformation continuing on from the reduced/recovered flow stress, following the flow stress/hardening rate law as described by Equation 7.3 (blue line Fig. 7.7). If this behaviour were observed experimentally, then separating the effects of precipitation and recovery (or the remaining forest hardening), in pre-deformed and aged Al-Mg-Cu samples, would be straight forward; the work hardening at yield would correspond to the forest hardening (dislocation) contribution to the flow stress, this being described by Equation 7.3. Knowing the dislocation contribution to the flow stress, as well as the other fixed contributions (e.g. solid solution, grain size), the precipitate contribution can be obtained as the remaining contribution to the overall yield stress, following the same approach taken in Chapter 6 (cf. Equation 6.3).

It is clear that this simple interpretation of the Kocks-Mecking model fails to adequately explain the work hardening changes that occur, following pre-deformation and aging in the Al-Mg-Cu and AA5252 alloys. This significantly complicates the separation of the cluster/GPB zone, and dislocation contributions, to the yield stress after pre-deformation and aging. Below the origins of these phenomena are discussed, and possible methods for predicting them by modifying the above described Kocks-Mecking model are
Figure 7.7: Schematic work hardening rate evolution. This a reproduction is based on the parameters used for the modeled Al-Mg alloy shown in Figure 7.6.

described.

The initial low work hardening rate observed in all pre-deformed and aged samples, has been previously reported for FCC materials, including aluminum, tested at temperatures lower than room temperature. This has been reported even for situations where the material has been pre-deformed, unloaded and then immediately re-loaded [179]. This effect has been referred to as the “unloading yield point effect” [179] or the “Hassen-Kelly effect” [180]. Different explanations for this behavior have been proposed, including the rearrangement of dislocations during unloading [180–182] and jog formation due to dislocation-vacancy interactions during unloading [179]. Regardless of the details, all of these mechanisms lead to a reduction in dislocations available to continue plastic deformation on re-loading. Few models exist to predict the mechanical consequences of this effect, Brown presenting a sophisticated mechanistic model for the Kelly-Haasen effect based on edge-dislocation dipole stability on unloading [182]. Further complicating the interpretation of the results presented here is that aging at elevated temperature is conducted in the present work. The effect observed here could therefore be described as a form of static strain aging though without the appearance of yield point phenomena typical of static strain aging in ferrous alloys [183]. Given that both alloys studied here have undergone static recovery, where dislocation rearrangement and solute redistribution has taken place, the density of dislocations could be significantly reduced by annihilation with other dislocations of opposite sign, or pinned by segregation of solute atoms as clearly shown in Chapter 6 for the case of the Al-Mg-Cu alloy (cf Figure 6.8).

Kubin et al. [184] have proposed that static strain aging can be described as being due to insufficient mobile dislocations to maintain the imposed plastic strain rate, the relationship between mobile dislocation
density \( (\rho_m) \) and the imposed strain rate \( \dot{\varepsilon} \) being given by,

\[
\dot{\varepsilon} = M \rho_m b v \tag{7.6}
\]

where \( v \) is the average dislocation velocity, which is assumed to be a power law of the applied stress. If \( \rho_m \) is low, then \( v \) must increase such that the imposed strain rate is met, this requiring a higher stress than what would be required if \( \rho_m \) was large.

Expanding Equation 7.6 considering thermally activated plastic deformation aided by the imposed stress, one can re-write it as \[185\],

\[
\dot{\varepsilon} = \dot{\varepsilon}_0 \left( \frac{\sigma}{\hat{\sigma}} \right)^{1/m} \tag{7.7}
\]

where \( \dot{\varepsilon}_0 \) is proportional to the mobile dislocation density and arrheniusly dependent on the deformation temperature, \( \hat{\sigma} \) is the limiting flow stress at zero imposed strain rate (or large \( \rho_m \)) and \( \sigma \) is the actual flow stress required to maintain the finite imposed strain rate. Finally, \( m \) is the rate sensitivity exponent.

In the case of the AA5252 (or any other solid solution strengthened alloy) the total flow stress can be written so as to incorporate this rate dependence \[177\]. The general additivity law can be written as \[154\],

\[
\sigma_{ys} = \sigma_0 + (\sigma_\perp^n + (\sigma_{ss}^n + \sigma_{ppt}^n)^{n/q})^{1/n} \tag{7.8}
\]

where \( \sigma_0 \) is the intrinsic and grain size contribution.

Under the same assumptions as described in Section 6.2.2, we can write Equation 7.8 as,

\[
\sigma = \sigma_\perp \left( \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \right)^m + \sigma_{ss} + \sigma_0 \tag{7.9}
\]

where \( \sigma_{ss} \) is the solid solution contribution to strength, and \( \sigma_0 \) is the contribution to the yield stress from the grain size and intrinsic strength. Moreover, \( \hat{\sigma} \) in this case can be taken as the forest strength given by the Taylor equation \( \sigma_\perp \).

Taking the derivative of Equation 7.9 with respect of the strain and using the chain rule gives,

\[
\theta = \frac{d\sigma}{d\varepsilon} = \left( \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \right)^m \left[ \frac{d\sigma_\perp}{d\varepsilon} - m \frac{\sigma_\perp}{\dot{\varepsilon}_0} \frac{d\dot{\varepsilon}_0}{d\varepsilon} \right] \tag{7.10}
\]

Written in this way it can be seen that the work hardening rate is composed of two terms. The first term \( (d\sigma_\perp/d\varepsilon) \) is the work hardening rate obtained in the rate insensitive limit, the one typically considered in the classic Kocks-Mecking approach. The second term is proportional to \(-d\dot{\varepsilon}_0/d\varepsilon\), the negative sign indicating that it acts to reduce the work hardening rate relative to that obtained in the rate insensitive limit. Recalling that \( \dot{\varepsilon}_0 \) is proportional to the mobile dislocation density, one can see that this term is related to how rapidly mobile dislocations are produced, in the rate sensitive regime (when \( \rho_m \) is low). In this regime, the flow stress will be reduced as new dislocations are produced, this reducing the macroscopic work hardening rate.

In the experiments reported here, one could expect this second term to be responsible for the initial
low work hardening rate following aging. Initially, following aging, the mobile dislocation density is low (owing to recovery and/or solute segregation) but as the material is deformed and dislocation sources begin to operate, the mobile dislocation density will quickly rise back to a level sufficient to satisfy Equation 7.6 meaning that \( \frac{d\dot{\epsilon}_0}{d\epsilon} \approx 0, \dot{\epsilon}_0 \approx \dot{\epsilon} \) and so the work hardening rate becomes the classic \( \frac{d\sigma}{d\epsilon} \).

The remaining problem is to obtain the evolution law for \( \dot{\epsilon}_0 \) (or equivalently, \( \rho_m \)). There have been several models proposed which attempt to predict evolution laws separately for the mobile and forest dislocation densities (so-called ‘two internal-state variable’ models) [177, 186]. These models require a large number of adjustable parameters, however, to describe the evolution law for both sets of dislocation as well as their interaction. Here, a much simpler approach is taken, motivated by the fact that the low work hardening regime appears only in the early stages of the deformation. From the picture envisioned here, dislocations sources will become active once plasticity starts again allowing the lost mobile dislocation density to be replaced by fresh mobile dislocations and a quick return to nearly rate insensitive behaviour. Here the simplest, empirical equation (Equation 7.11) is proposed,

\[
\frac{d\dot{\epsilon}_0}{d\epsilon} = \eta \left(1 - \frac{\dot{\epsilon}_0}{\dot{\epsilon}}\right)
\]  

(7.11)

this expression linearly reduces \( d\dot{\epsilon}_0/d\epsilon \) as a function of \( \dot{\epsilon}_0 \) until \( \dot{\epsilon}_0 = \dot{\epsilon} \).

The advantage of such a simple expression is that it adds only two adjustable parameters, \( \eta \) and the initial value of \( \dot{\epsilon}_0 = \dot{\epsilon}_0^0 \), to describe the evolution of the mobile dislocation density/\( \dot{\epsilon}_0 \) and thus the transient work hardening behaviour.

Figure 7.8 illustrates the results obtained when the work hardening rate is predicted using Equations 7.10 and 7.11, with \( \frac{d\sigma}{d\epsilon} \) being given by the parameterized Kocks-Mecking model used in Figure 7.6. While this allows for the initial, transient low work hardening behaviour to be explained, it does not provide an explanation for the higher than expected work hardening rate (and non-linear work hardening rate evolution), observed over the rest of the flow curve (cf. Figure 7.5).

In the above discussion, it was assumed that the mobile dislocation density was reduced through the processes of recovery and/or solute segregation to dislocations, with segregation to dislocations having been observed for the case of the Al-Mg-Cu alloy in Chapter 6. It has been shown theoretically, for the case of Al-Mg alloys, that the stress to de-pin a dislocation (edge or screw) from a fully formed solute atmosphere can be much higher than the flow stresses measured experimentally here [98]. This would suggest that these dislocations are not only immobile during deformation but that they will also be difficult to recover dynamically during plastic deformation. Such segregated forest dislocations should contribute to the generation of new forest dislocations (the first term in Equation 7.1) but that they will not be available for dynamic recovery (the second term in Equation 7.1). This portion of the dislocation density, fixed by the level of pre-deformation, the level of recovery and the aging treatment, must be treated separately from the conventional forest dislocation density in Equation 7.1,

\[
\frac{d\rho}{d\epsilon^p} = k_3 \sqrt{\rho} - k_2 \rho + k_3 \rho_{pinned}
\]  

(7.12)
Figure 7.8: Representation of the modeled deformation accounting for an initial low mobile dislocation density, on the work hardening evolution represented by the Kocks-Mecking plot. The vertical line at the beginning of pre-strain curve represent the end of the elastic segment. The representation was done using $k_1 = 5.64 \times 10^8 \ [1/m]$, $k_2 = 9.41$ ($k_1$ and $k_2$ as obtained from the continuously deformed AA5252 alloy), $\eta = 0.08$, $\varepsilon_{0,i} = 1 \times 10^{-4}$ and $\sigma_{\perp,i} = 200 \ [MPa]$

where a separate constant $k_3$ is defined (rather than assuming it to be equal to $k_2$) to reflect the fact that the interaction with segregated dislocations may be different from those that are free of segregation. In the tests performed in this work, it is expected that $\rho_{\text{pinned}}$ will be an unknown constant for a given level of pre-deformation and a given aging condition. Thus we can replace $k_3 \rho_{\text{pinned}}$ with a single constant, $k_D$ considering the prediction of the work-hardening response for a single stress-strain curve. In this case, a modified version of the Kocks-Mecking model can be written,

$$\frac{d\sigma_{\perp}}{d\varepsilon^p} = \theta_0 \left( 1 - \frac{\sigma_{\perp}}{\sigma_{\varphi}} \right) + \frac{k_D (\alpha M G b)^2}{2\sigma_{\perp}} \ (7.13)$$

Its important to note that Equation 7.13 has been commonly used to describe the effect of non-shearable obstacles to dislocation motion in the context of precipitation hardened alloys [187, 188]. In this context, the second term in Equation 7.13 represents the additional storage of geometrically necessary dislocations.

The effect of this addition term in the Kocks-Mecking model can be observed in Figure 7.9 where Equation 7.13 is plotted based on the behaviour of the AA5252 alloy shown in Figure 7.6. Here the blue curve shows the baseline case ($k_D = 0$ as in Figure 7.9). The black and red curves imagine a situation where the material has been pre-deformed to $\Delta \sigma = 200 \ [MPa]$. The red line then shows the predicted effect
of continuing to deform but now when \( k_D = 1 \times 10^{15}[1/m^2] \). It can be seen that the work hardening rate following reloading is higher than what it was at the end of the pre-deformation due to the extra generation of dislocations due to the second term in Equation 7.13, but that the work hardening rate of the red curve approaches that of the blue curve as the flow stress increases.

![Graph](image.png)

**Figure 7.9:** Effect of additional term for the generation of dislocations during plastic deformation, on the work hardening evolution represented by the Kocks-Mecking plot. This curve was constructed using the following parameters: \( k_D = 1 \times 10^{15}[1/m^2] \), \( k_1 = 5.64 \times 10^8 [1/m] \), \( k_2 = 9.41 \), and \( \sigma_{\perp,i} = 200 \text{ [MPa]} \). The vertical lines at the beginning of each plot represent the end of the elastic segment.

Finally, the two models derived here can be used to describe the overall behaviour observed experimentally in this chapter. Figure 7.10 shows the results of Equations 7.10 and 7.11 combined with \( d\sigma_\perp/d\varepsilon \) being given by Equation 7.13 parameterized as shown in Figure 7.9. One can see that the two deviations from the classic Kocks-Mecking model observed for the Al-Mg-Cu alloy and the AA5252 are qualitatively reproduced by this modified model. In the following, an attempt is made to compare this modified model to the experiments and to finally extract from the model the separate effects of cluster/GPB zone hardening and recovery softening in the Al-Mg-Cu alloy.
Figure 7.10: Effect of additional term for the generation of dislocations, and low initial mobile dislocation density during plastic deformation, on the work hardening evolution represented by the Kocks-Mecking plot. This curve was constructed using the following parameters: $k_D = 1 \times 10^{15} [1/m^2]$, $k_1 = 5.64 \times 10^8 [1/m]$, $k_2 = 9.41$, $\eta = 0.08$, $\varepsilon_{0,i} = 1 \times 10^{-4}$, and $\sigma_\perp = 200$ [MPa]. The vertical line at the beginning of the pre-strain plot represents the end of the elastic segment.

7.3 Predicting the Effect of Recovery on Work Hardening for the AA5252 Alloy

As a first step towards analyzing the Al-Mg-Cu alloy, the simpler case of describing the work hardening response of the AA5252 alloy using the model developed above is first explored.

The full model (Equations 7.10, 7.11 and 7.13) requires knowledge of several parameters, some of which are constants that can be determined from a single experiment, others which vary with the pre-deformation and aging conditions.

The parameters $k_1 = 5.64 \times 10^8$ m$^{-1}$ and $k_2 = 9.41$ set the work hardening rate of the non-pre-deformed sample, these having been previously determined in Figure 7.6. These parameters are fixed independent of the pre-deformation/aging conditions.

The remaining parameters for the model, all dependent on the pre-deformation and aging conditions are;

1. The initial value of $\dot{\varepsilon}_{0,i}$
2. The rate of mobile dislocation generation, $\eta$
3. The work hardening parameter $k_D$

4. The initial stress contribution due to work hardening, this due to the retained dislocations after recovery, $\sigma_{\perp,i}$

Manually finding the best fit values for these four parameters is made easier by the fact that the first two only modify the very initial portion of the work hardening plot (the low work hardening transient), while the third dominates the shape of the work hardening evolution over most of the rest of the curve, and the fourth determines the beginning of the curve.

Figure 7.11 shows an example of the model fit to the experimental data for the AA5252 alloy pre-deformed by $\Delta \sigma = 174$ MPa, and then aged at $200^\circ$C for 2 minutes. The remaining modeled vs. experimentally obtained Kocks-Mecking plots can be consulted in Appendix F. One can see that this rather simple model is able to successfully predict the shape of the work hardening curve, though it does not perfectly match the initial low hardening rate transient. This is likely a consequence of the simplified approach to predicting the evolution of $\dot{\varepsilon}_0$.

![Figure 7.11: Experimental and modeled Kocks-Mecking representation of AA5252 (Al-2.94 at.% Mg) system, pre-deformed $\Delta \sigma=174$ MPa, aged 2 min at 200 °C, and further re-strained.](image)

The best fit parameters obtained for all of the aging conditions explored for the AA5252 alloy (i.e. pre-deformation to $\Delta \sigma= 44$ MPa, and $\Delta \sigma= 174$ MPa and aging at 160 and 200 °C) are given in Table 7.1.

It was found that it was possible to fit the initial low work hardening rate transient by fixing one of $\eta$ or $\dot{\varepsilon}_0$, and varying the other as a function of the pre-deformation and aging conditions. Here $\eta=0.08 \ [1/s]$ was...
Table 7.1: Numerical values of parameters used in fitting the work hardening model to the work hardening response of the AA5252 alloy following pre-deformation and aging. In all cases $k_1 = 5.64 \times 10^8$ m$^{-1}$ and $k_2 = 9.41$.

<table>
<thead>
<tr>
<th>Aging Time (minutes)</th>
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<th>2</th>
<th>5</th>
<th>30</th>
<th>420</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \sigma = 44$ MPa, $T = 160^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\perp,i}$ MPa</td>
<td>42</td>
<td>38</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\dot{\varepsilon}_{\text{ii}}$ s$^{-1}$</td>
<td>$1.4 \times 10^{-5}$</td>
<td>$9 \times 10^{-5}$</td>
<td>$1.3 \times 10^{-5}$</td>
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</tr>
<tr>
<td>$k_D$ m$^{-2}$</td>
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<td>$0.5 \times 10^{15}$</td>
<td>$0.5 \times 10^{15}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta$ s$^{-1}$</td>
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<td>0.08</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta \sigma = 44$ MPa, $T = 200^\circ$C</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\sigma_{\perp,i}$ MPa</td>
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<td>51</td>
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<td></td>
</tr>
<tr>
<td>$\eta$ s$^{-1}$</td>
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<td>0.08</td>
<td>0.08</td>
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<td></td>
</tr>
<tr>
<td>$\Delta \sigma = 174$ MPa, $T = 160^\circ$C</td>
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<td>$\sigma_{\perp,i}$ MPa</td>
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<td>113</td>
<td>108</td>
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<tr>
<td>$\dot{\varepsilon}_{\text{ii}}$ s$^{-1}$</td>
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<td>$6 \times 10^{-5}$</td>
<td>$6.5 \times 10^{-5}$</td>
<td>$3 \times 10^{-5}$</td>
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<tr>
<td>$k_D$ m$^{-2}$</td>
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<td>$1.5 \times 10^{15}$</td>
<td>$0.5 \times 10^{15}$</td>
<td>$1.5 \times 10^{15}$</td>
<td>$1.5 \times 10^{15}$</td>
</tr>
<tr>
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<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>$\Delta \sigma = 174$ MPa, $T = 200^\circ$C</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\perp,i}$ MPa</td>
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<td>105</td>
<td>104</td>
<td></td>
<td></td>
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<tr>
<td>$\dot{\varepsilon}_{\text{ii}}$ s$^{-1}$</td>
<td>$9.4 \times 10^{-5}$</td>
<td>$10.5 \times 10^{-5}$</td>
<td>$13.0 \times 10^{-5}$</td>
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<td></td>
</tr>
<tr>
<td>$k_D$ m$^{-2}$</td>
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<td>$1.5 \times 10^{15}$</td>
<td>$1.5 \times 10^{15}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta$ s$^{-1}$</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

fixed to be constant for all conditions, and the value of $\dot{\varepsilon}_{\text{ii}}$ was varied as shown in Table 7.1. Owing to the simplistic nature of the model for the variation of $\dot{\varepsilon}_0$, and its inability to perfectly match the experimentally observed low work hardening rate transient, it is difficult to infer a physical explanation for the variation of $\dot{\varepsilon}_{\text{ii}}$ with pre-deformation or aging.

In the case of $k_D$, it was found that a good fit to the data was obtained when a single value of $k_D$ was chosen for a given level of pre-deformation, the value of $k_D$ increasing with the level of pre-deformation. The fact that $k_D$ increases with the level of pre-deformation would be consistent with the model developed above which predicted that $k_D$ should be proportional to the density of dislocations pinned by solute segregation. The independence of $k_D$ with the aging time and temperature could also be consistent with the fact that even a small amount of segregation is sufficient to increase the stress required for de-pinning [98]. In this case, the immobilized dislocations would be formed within the first few minutes of aging at 160 and 200°C.
7.3.1 Separating the Effects of Cluster/GPB Zone Hardening and Recovery Softening in the Al-Mg-Cu alloy

The original aim of this analysis was to determine, from the measurement of yield strength and work hardening rate alone, the contributions of forest hardening and cluster/GPB zones strengthening in the Al-Mg-Cu alloys, and to identify whether it is a reduction in the rate of softening by recovery due to pinning of dislocations [120], or cluster/GPB zone hardening alone, which allows for this material to retain its strength during the paint bake cycle. Here, the model developed above is used to fit the work hardening behaviour of the material and to, therefore, allow for this question to be answered.

Compared to the analysis of the AA5252 alloy, cluster/GPB zone hardening must be included into the analysis. This is done by modifying Equation 7.9 to,

\[
\sigma = \sigma_0 (\dot{\varepsilon} / \dot{\varepsilon}_0)^n + \sqrt{\sigma_{ss}^2 + \sigma_{ppt}^2} \quad (7.14)
\]

As described in Section 6.2.2, the key assumption in the use of such an addition law, is that solute and clusters/GPB zones are assumed to have similar strengths (Chapter 5), while the strength arising from dislocations is assumed to be considerably larger (6). As a starting point, based on the work in Chapter 5, it is assumed that the clusters/GPB zones contribute only to the yield strength, and not to the work hardening rate of the alloy. In this case the cluster/GPB zone strength (\(\sigma_{ppt}\)) is taken as an adjustable parameter in the model. The contribution of solute in solid solution \(\sigma_{ss}\) has been considered to be constant, this consistent with the observation made in Chapter 5.

As in the case of the AA5252 alloy, five additional parameters must be fit for each of the aging conditions studied (Table 7.2). From the as-solution treated stress-strain curve, the values of \(k_1 = 6.55E+08 \text{ m}^{-1}\) and \(k_2 = 9.97\) were fixed (Figure 7.6). As in the case of the AA5252 alloy, it was found that the value of \(\eta\) could be fixed to a constant value of 0.08 s\(^{-1}\) for all conditions, while \(\dot{\varepsilon}_0\) was varied with pre-deformation and aging conditions, the values of this parameter being given in Table 7.2. Although the values of \(\dot{\varepsilon}_0\) found for this alloy are not identical to those found for the AA5252 alloys, they result very similar. This is not surprising given that the mechanism envisioned does not depend on precipitation, and thus should not be strongly dependent on the small difference in Cu and Mg content of the alloys.

Also consistent with the concept of this model is the fact that the same values of \(k_D\), used for the AA5252 alloy, could be successfully used here, with \(k_D = 0.5 \times 10^{15}\) for \(\Delta \sigma = 44\) MPa, and \(k_D = 1.5 \times 10^{15}\) for \(\Delta \sigma = 174\) MPa.

Figure 7.12 shows an example of the model fit to the work hardening response of an Al-3.23 at.% - 0.23 at.%Cu alloy sample, pre-deformed to \(\Delta \sigma = 174\) MPa, and aged for 2 minutes at 200\(^\circ\)C. The fits to the other test conditions are being provided in Appendix F.

While nearly all of the tested conditions were found to be adequately fit using the approach described above, the samples pre-deformed to \(\Delta \sigma = 44\) and 174 MPa and then aged for 420 min at 200\(^\circ\)C, provided uniquely poor fits. Figure 7.13 shows that, unlike the shorter aging times, the experimental response at this longer aging time appears to fall back towards the as-solution treated work hardening curve faster. In the
Table 7.2: Numerical values of parameters used in fitting the work hardening model to the work hardening response of the Al-3.23 at.% - 0.23 at.%Cu alloy following pre-deformation and aging. In all cases $k_1 = 6.55 \times 10^8$ m$^{-1}$ and $k_2 = 9.97$. Note that the fit obtained for both conditions aged for 420 minutes at 200°C gave less satisfactory fits to the model compared to the other conditions.

In fitting the above model, it was possible to obtain the value of $\sigma_{ppt}$ and the value of $\sigma_{\perp,i}$, at the onset of...
Figure 7.12: Experimental and modeled Kocks-Mecking representation of Al-3.23 at.% - 0.23 at.%Cu alloy system, deformed $\Delta \sigma = 174$ MPa, aged 2 min at 200 °C.

Figure 7.13: Kocks-Mecking plot for Al-3.23 at.% - 0.23 at.%Cu aged at 200 °C, pre-deformed a) $\Delta \sigma = 44$ MPa, and b) $\Delta \sigma = 174$ MPa.

yielding ($\sigma$). The former is the cluster/GPB zone strength, while the latter is the remaining forest hardening following recovery. Starting with the variation of $\hat{\sigma}_0$ (Figure 7.14), it is seen that it remains (to within the accuracy obtainable from the fits to the model) constant and independent of aging time. Also plotted in Figure 7.14 is the data obtained directly from the AA5252 alloy. This is the same data used to approximate
the recovery rate of the Al-Mg-Cu alloy in the analysis performed in Chapter 6. It can be seen that the approximation is good, with the forest contribution to the flow stress in the two alloys being nearly identical for both levels of pre-strain and for both aging temperatures. The observed recovery in Al-Mg-Cu exhibits the same quick drop, showing no further evolution as seen in AA5252 alloy and can be rationalized as done in Section 6.2.2.

The similarity in the forest contribution to the flow stress for the Al-Mg-Cu and AA5252 alloy suggests that the analysis performed here should give very similar predictions for the contribution of $\sigma_{ppt}$ to the yield strength of the aged samples as well. Indeed, as shown in Figure 7.15 the results obtained through the application of the model proposed here give nearly identical results to those presented via the much simpler analysis performed in Chapter 6 (cf. Figure 6.6). Importantly it is found here that for aging at 160°C and 200°C the initial cluster/GPB zone contribution to the strength is lower than what it would be for aging of the as-solutionized sample. Moreover, it is seen (for both aging temperatures) that the magnitude of the pre-deformation has little effect on the aging response. Finally, it is noted that while the overall, contribution of $\sigma_{ppt}$ is lower for the pre-deformed samples, the rate of increase in $\sigma_{ppt}$ is the same in all cases.

One of the key questions posed at the outset of this thesis was whether the observed suppression of softening of AA5XXX alloys during the paint bake cycle due to the minor addition of Cu was due to a retardation of recovery (owing to pinning of dislocations) or due to cluster/GPB zone hardening. The results presented in this Chapter (as well as the one before it) provide strong evidence that recovery is affected very little by the addition of Cu and that the improved performance in the paint bake cycle arises from cluster/GPB zone induced hardening that can more than counterbalance the loss in strength arising from the recovery. The fact that there is only a minor coupling between the process of clusters/GPB zone formation and recovery makes alloy design and selection significantly easier. Though pre-deformation may lower the effect of cluster hardening relative to what is achievable in the aging of the as-solutionized material, there may be ways to modify this (as explained in Chapter 6) by modifying the processing conditions to control the excess vacancy concentration. Moreover, while the exact mechanism leading to the linear dependence of $\sigma_{ppt}$ with the logarithm of aging time remains only hypothesized, this observation provides a way of predicting the hardening response of other, similar, alloys with a minimum number of experiments.

### 7.4 Summary

The key observations and conclusions from this Chapter can be summarized as follows:

- In this chapter the mechanical response of the Al-3.23 at.% - 0.23 at.%Cu and AA5252 alloys were analyzed using a modified version of the Kocks-Mecking model with the aim of independently verifying the separate contributions of forest hardening and cluster/GPB zone strength in the pre-deformed and aged Al-3.23 at.% - 0.23 at.%Cu alloy.

- It was found that a simple application of the Kocks-Mecking analysis failed to predict the basic work hardening behaviour of either alloy following pre-deformation and aging.
• Two modifications were made to the classic Kocks-Mecking analysis, so as to account for the effects of solute segregation to dislocations, these acting to modify the available mobile dislocation density at the onset of yielding and to provide additional dislocation obstacles throughout the entire stress-strain curve.

• Using the previously mentioned approach, the work hardening behaviour for both alloys was successfully modelled. The results of this model were used to estimate the cluster/GPB zone and dislocation forest contributions to the yield strength, the results obtained here independently confirming those hypothesized in the previous chapter.

• Importantly, it is confirmed through this analysis that i) recovery is negligibly affected by the cluster/GPB zone formation and that ii) pre-deformation suppresses a portion of the rapid initial cluster hardening that is observed in aging of the as-solution treated samples.
Figure 7.14: Forest strength from conversion of extracted dislocation density for Al-3.23 at.% - 0.23 at.% Cu aged at (a) 160 °C and (b) 200 °C, pre-strained $\Delta \sigma = 44$ MPa, and $\Delta \sigma = 174$ MPa.
Figure 7.15: Precipitation contribution to the total strength for Al-3.23 at.% - 0.23 at.%Cu aged at a) 160 °C and b) 200 °C, pre-strained $\Delta \sigma = 44$ MPa, and $\Delta \sigma = 174$ MPa. These results have been plotted along the precipitation contribution for material without any pre-deformation as calculated in Section 6.2.2.
Chapter 8

Summary and Conclusions

In this thesis, the relation between concurrent recovery and precipitation in a pre-deformed Al-Mg-Cu alloy was studied with the aim of identifying how these processes affect the material’s yield strength during conditions compatible with the industrial automotive paint bake cycle. While it had been previously shown that small additions of Cu could reduce softening of AA5XXX series alloys during simulated paint bake processes, the origins of this phenomenon remained unexplored.

Due to the limited body of literature dedicated to low Cu Al-Mg-Cu system, it was necessary to first characterize the precipitation process taking place after solution treatment. Chapter 5 was dedicated to this purpose, using macroscopic characterization techniques, specifically, electrical resistivity, DSC and detailed uniaxial tensile tests. Furthermore, microscopic characterization of the precipitation process was possible by using Atom Probe Tomography (APT). The use of APT revealed that, under the times and temperatures relevant to the paint bake cycle, the age hardening observed during artificial aging is the result of solute clusters/GPB zones. The presence of these clusters/GPB zones was shown to be consistent with the observed changes in electrical resistivity and DSC.

A new cluster analysis technique for interpreting APT data, based on pair correlation functions, was used to obtain quantitative information about clusters/GPB zones. The output of this analysis was then used as input to a detailed yield strength model, showing that the age hardening response is due to a bimodal distribution of features which evolve differently during aging. While it has been previously hypothesized that the clusters/GPB zones found in low Cu:Mg alloys are the same as those found in more conventional AA2XXX alloys, here it was shown that the clusters/GPB zones contained very little Cu, with the two majority species being Al (~80%) and Mg (~15-20%). This helps to explain how efficient the very small additions of Cu are in producing age hardening comparable to that found in much more Cu rich AA2XXX alloys.

The particular age hardening kinetics observed in these alloys was hypothesized to be a result of coarsening. While a detailed model of cluster/GPB zone growth would require more detailed information about the thermodynamics and crystallography of these features, a simple phenomenological model was proposed that can be used (upon parameterization) to predict the age hardening response. This analysis could be
useful for future rapid alloy design experiments.

With this understanding of the age hardening response in solution treated materials, Chapter 6 focused on the more industrially relevant processes involved in aging of samples that had be pre-deformed plastically. The key finding from this Chapter was that pre-deformation reduced the immediate jump in yield strength experienced during the first 1-2 minutes of aging. The kinetics of aging following this, however, were seen to be unaffected by pre-deformation. Microstructure characterization, though much more difficult in these samples, revealed a reduction in the presence of small clusters/GPB zones compared to the microstructure of the as-solution treated material aged for the same time. Prominent in APT observations was segregation interpreted as segregation along dislocations. It was proposed that the reduction in age hardening response at short times was due to the rapid annihilation of excess vacancies to dislocations, vacancies being an important contributor to the formation and growth of clusters/GPB zones. A simple model was used to illustrate the importance of dislocations on the rate of loss of vacancies.

In the final Chapter, a method was proposed to separate the effects of cluster/GPB zone hardening and recovery induced softening by an analysis of the work hardening response of pre-deformed and aged samples. It was shown that a simple application of the Kocks-Mecking model was insufficient to explain the shape of the stress-strain curve (work hardening behaviour) following aging of the pre-deformed material. For this reason, two new ingredients were added, one dealing with the loss of mobile dislocations during aging and the second considering dislocations pinned by solute (as revealed in APT observations) as fixed obstacles during subsequent deformation. Using this revised model, it was possible to show that recovery proceeds very rapidly for the aging conditions examined such that there is no strong coupling between recovery and cluster/GPB zone formation. This analysis also confirmed the approximate analysis performed in the previous chapter showing that the cluster/GPB zone hardening in the pre-deformed samples is reduced during the first minutes of aging. The application of the methodology developed in this chapter to separating the effects of age hardening and recovery softening should be valuable for the analysis of other alloys where precipitation and recovery are coupled.

8.1 Future work

The results of this thesis raise many new possible directions for future research. Below, four are suggested. **Identification of the Structure and Thermodynamics Governing the Clusters/GPB zones**

The study of the detailed structure and thermodynamics of the clusters/GPB zones observed here was outside the scope of this work. Further work, however, requires more detailed experimental and theoretical study of the structure and composition of these ‘phases’. The experimental results presented here suggest that the composition of these ‘phases’ is much higher in Al than previous studies have shown. This presents a challenge for electron microscope characterization but with improvements in techniques it has been suggested that this might be possible. Quantum mechanical calculations able to assess the stability of a large number of structures in the composition range observed here would also be very valuable. **Characterization and Modelling of the Kinetics of Aging:**
It has been hypothesized here that the aging kinetics are controlled by a coarsening-like process. Given the complexity of the microstructure of these alloys this requires further exploration with the aim of providing a more physical explanation of the aging kinetics. This analysis would greatly benefit from measurement of the volume fraction, size and composition of the clusters/GPB zones for a wide range of different aging temperatures and times. While detailed APT analysis could provide this data, the cost (in time) would be very high and statistics would be a question. New developments in small angle x-ray scattering analysis could also provide a route for a more rapid method to perform this sort of analysis despite the low chemical contrast between Al and Mg.

**Effect of Excess Vacancy Concentration on Aging:**

It has been proposed that the aging of the Al-Mg-Cu alloy is highly sensitive to the vacancy concentration, particularly in the first seconds of aging. This should be further studied by varying the excess vacancy concentration at the beginning of aging. This could be achieved by adopting different solution treatment temperatures and/or quenching rates. If results show a clear sensitivity to the change in vacancy density, industrial strategies to induce a higher strengthening response in these alloys could be envisioned. These could include the addition of solute atoms that can trap vacancies or by the recent cyclic deformation mechanism [189].

**Application of Work Hardening Model to Other Conditions:**

The modeling strategy developed in the final chapter was shown to allow for the separation and quantification of the effects of retained work hardening and clustering. This approach should be tested against a range of other alloys/test conditions to evaluate the breadth of its applicability. For example, it could be applied to samples pre-deformed at room temperature, this being closer to the condition experienced in industry.
Bibliography


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Appendix A

No Deformed Al-Mg-Cu alloy: Complementary Mechanical Characterization Data

The full set of stress vs. strain and Kocks-Mecking plots, corresponding to the Al-3.23 at.%-0.23 at.%Cu alloy, aged at 200 and 160 °C, are shown next.

![Stress vs. strain plot](image)

**Figure A.1:** Stress vs. strain evolution of Al-3.23 at.%-0.23 at.%Cu alloy during artificial aging at 200 °C,
Figure A.2: Kocks-Mecking plot evolution of Al-3.23 at.%-0.23 at.%Cu alloy during artificial aging at a) 200 °C,

Figure A.3: Stress vs. strain evolution of Al-3.23 at.%-0.23 at.%Cu alloy during artificial aging at 160 °C,
Figure A.4: Kocks-Mecking plot evolution of Al-3.23 at.%-0.23 at.%Cu alloy during artificial aging at a) 200 °C,
Appendix B

Resistivity in Solid Solution State

Resistivity measurements after solid solution treatment were analyzed using the reported coefficients for alloying elements in solid solution in Al measured at 77K as the measurements performed in this thesis work [190], assuming a resistivity behaviour as given by the Matthiessen’s rule [127], measured in the conditions and over the material described in the Methodology (Chapter 4). The same coefficients have been used in previous research performed in the same instrumentation as used in this work [134].

The theoretical values are consistent with the experimentally obtained values (Table B.4), when no Fe contribution is accounted in solid solution. This is compatible with the presence of Fe rich constitutive particles (e.g. Al₃Fe).

<table>
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</tr>
</thead>
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</tr>
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<tr>
<td>Ti</td>
<td>0.008</td>
<td>55.63</td>
<td>0.47</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>Balance</td>
<td>-</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Total - Fe included 25.83

Total - No Fe included 21.97

Table B.1: Resistivity contributions from solute elements in solid solution in Al-3.23 at.% Mg-0.23 at.%Cu alloy. The contribution of minor alloying elements is not considered.
### Table B.2: Resistivity contributions from solute elements in solid solution in Al-3.2 at.% Mg - 0.12 at.% Cu alloy. The contribution of minor alloying elements is not considered.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Concentration [at.%]</th>
<th>Coefficient [nΩ m/at.%]</th>
<th>Resistivity contribution [nΩ m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>3.2</td>
<td>5.27</td>
<td>16.9</td>
</tr>
<tr>
<td>Cu</td>
<td>0.115</td>
<td>7.98</td>
<td>0.92</td>
</tr>
<tr>
<td>Fe</td>
<td>0.046</td>
<td>79.06</td>
<td>3.71</td>
</tr>
<tr>
<td>Si</td>
<td>0.046</td>
<td>6.55</td>
<td>0.42</td>
</tr>
<tr>
<td>Ti</td>
<td>0.007</td>
<td>55.63</td>
<td>0.42</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al Balance</td>
<td>-</td>
<td>-</td>
<td>2.29</td>
</tr>
<tr>
<td>Total - Fe included</td>
<td></td>
<td></td>
<td>24.54</td>
</tr>
<tr>
<td>Total - No Fe included</td>
<td></td>
<td></td>
<td>20.83</td>
</tr>
</tbody>
</table>

### Table B.3: Resistivity contributions from solute elements in solid solution in Al-2.9 at.% Mg alloy. The contribution of minor alloying elements is not considered.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Concentration [at.%]</th>
<th>Coefficient [nΩ m/at.%]</th>
<th>Resistivity contribution [nΩ m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>2.93</td>
<td>5.27</td>
<td>15.48</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0008</td>
<td>7.98</td>
<td>0.006</td>
</tr>
<tr>
<td>Fe</td>
<td>0.031</td>
<td>79.06</td>
<td>2.47</td>
</tr>
<tr>
<td>Si</td>
<td>0.044</td>
<td>6.55</td>
<td>0.28</td>
</tr>
<tr>
<td>Ti</td>
<td>0.006</td>
<td>55.63</td>
<td>0.34</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al Balance</td>
<td>-</td>
<td>-</td>
<td>2.29</td>
</tr>
<tr>
<td>Total - Fe included</td>
<td></td>
<td></td>
<td>20.89</td>
</tr>
<tr>
<td>Total - No Fe included</td>
<td></td>
<td></td>
<td>18.42</td>
</tr>
<tr>
<td>Alloy</td>
<td>Mean Resistivity [nΩ m]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al - 3.35 at.% Mg 0.23 at.% Cu</td>
<td>22.1 ± 0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al - 3.2 at.% Mg 0.12 at.% Cu</td>
<td>21.4 ± 0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al - 2.9 at.% Mg</td>
<td>18.1 ± 0.19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table B.4:** Average resistivity values experimentally obtained after solid solution treatment.
Appendix C

Radial Distribution Function and Pair Correlation Function (PFC)

The Radial Distribution Function (RDF) can be obtained directly from APT dataset, this function is defined as:

\[ g_{ij}(r) = \frac{C_{ij}(r)}{C_{0,j}} \] (C.1)

where \( C_{ij} \) is the average concentration of "j" atoms located at a distance "r" from a "i" atom, and \( C_{0,j} \) is the average concentration of "j" atoms in the material. From here we will assume an isotropic system.

From the definition of PCF given in Chapter 5 (Equation 5.1), we can appreciate the relationship between the RDF and the PCF as,

\[ \gamma_{ij}(r) = C_{0,j}C_{ij}(r) - C_{0,i}C_{0,j} \]
\[ = \frac{g_{ij}(r)}{c_{0,j}} - 1 \] (C.2)

Furthermore, from Eq. 5.2, we can separate the composition and volume fraction contribution from the geometrical contributions. Assuming that the RDF function is constructed from B solute atoms from the nearest neighbors (binary A-B system) contained in a volume \( dV \) \((r \approx 0)\), we can rewrite,

\[ \gamma_{ii}(0) = \gamma_{ii}(0) = \frac{g_{ii}(0)}{c_{0,i}^l} - 1 \] (C.3)

Where \( g_{ii}(0) \) is only function of the local concentration and volume fraction. We can further define this, based on the weighted contribution of concentration contribution in \( dV \) as,

\[ \frac{g_{ii} dV}{c_{0,i}^l} = \frac{p(\beta)C_{\beta}dV + p(\alpha)C_{\alpha}dV}{c_{0,i}^l} \] (C.4)

Where \( p(\beta) \) and \( p(\alpha) \) are the probability of the volume \( dV \) of be located in the \( \beta \) phase and \( \alpha \) phase,
respectively. These probabilities can be defined as,

$$p(k) = \frac{N_B^k}{N_B}, \quad k = (\alpha, \beta) \quad (C.5)$$

Where $N_B^k$ is total number of B atoms in the $k$ phase, and $N_B$ is the total number of B atoms in the material. We can express these probabilities in terms of the volume fraction as,

$$p(k) = \frac{N_B^k}{N_B} = \frac{f_k^C N_B}{C_0}, \quad k = (\alpha, \beta) \quad (C.6)$$

Substituting in Eq. C.4 results in,

$$g_{ii}C_i^0 = \left( f_\beta v C_\beta^2 + f_\alpha v C_\alpha^2 \right) C_0^2 \quad (C.7)$$

From the definition given in Eq. C.3,

$$\gamma_{-i}(0) = \frac{g_{ii}}{C_0^j} - 1 = \frac{\left( f_\beta v C_\beta^2 + f_\alpha v C_\alpha^2 \right)}{C_0^2} - \frac{C_0^2}{C_0^2} = \frac{C_0^2}{C_0^2} \quad (C.8)$$

This expression can be further simplified by taking advantage of the fact that $C_0 = C_\beta f_\beta v + C_\alpha f_\alpha v$, resulting in:

$$\gamma_{-i}(0) = \frac{f_\beta v f_\alpha v (C_\beta - C_\alpha)^2}{C_0^2} \quad (C.9)$$

Which is Eq. 5.4, used in Section 5.1.5. The previous rationale can be extended for two solute components, giving origin to Eq. 5.5 in the previously mentioned Section.
Appendix D

Pair Correlation Function Fit

As mentioned in Section 5.1.5, the experimentally obtained pair correlation functions do not result proportional to each other, this compatible with the idea of different distributions of clusters contribution to the constructed PCF’s. To tackle this problem, two PCF’s are proposed to be represent the experimentally obtained PCF’s. Taking advantage of the capacity to separate the geometrical contribution $\gamma_j (r)$, and the chemical contribution $\gamma_j (0)$, to the total PCF (Eq. 5.2), we can perform two separated fitting procedures. For the first case, the chemical contributions ($\gamma_j (0)$), we propose a system of equations associated to each experimentally obtained $\gamma_j (r)$ as,

$$\begin{align*}
\gamma^\text{Tot}_{\text{CuCu}} (0) &= \gamma^D_1 \gamma^\text{Tot}_{\text{CuCu}} (0) + \gamma^D_2 \gamma^\text{Tot}_{\text{CuCu}} (0) \\
\gamma^\text{Tot}_{\text{MgMg}} (0) &= \gamma^D_1 \gamma^\text{Tot}_{\text{MgMg}} (0) + \gamma^D_2 \gamma^\text{Tot}_{\text{MgMg}} (0) \\
\gamma^\text{Tot}_{\text{CuMg}} (0) &= \gamma^D_1 \gamma^\text{Tot}_{\text{CuMg}} (0) + \gamma^D_2 \gamma^\text{Tot}_{\text{CuMg}} (0)
\end{align*}$$  

(D.1)

Where $D_1$ and $D_2$ indicates distribution 1 and 2, respectively, and each $\gamma_j (0)$ is given by either Eq.5.4 or Eq.5.4. The local matrix composition has been obtained from the APT datasets using the DIAM protocol [191], for both aging times. Each distribution is assumed to fulfill the mass balance within each proposed distribution, namely,

$$\begin{align*}
1 &= 0.8 + C^D_{\text{Cu}} + C^D_{\text{Mg}} \\
1 &= 0.8 + C^D_{\text{Cu}} + C^D_{\text{Mg}}
\end{align*}$$  

(D.2)

Where the assumption of a 80at.\% concentration of Al in the cluster has been preserved. And, finally, from Eq. 5.6,

$$\gamma^\text{Tot}_{\text{CuMg}} (0) = \sqrt{\gamma^\text{Tot}_{\text{CuCu}} (0) \gamma^\text{Tot}_{\text{MgMg}} (0)}$$  

(D.3)

This proposed non-linear system of equations can be solved using a numerical equation solver routine. From this strategy, we are able to obtain the volume fraction and mean solute concentration of each proposed particle size distribution.

Regarding the geometrical contribution $\gamma_0 (r)$, a solution is obtained by simultaneously fitting the pair
correlation function obtained from the Cu-Cu, Mg-Mg, and Cu-Mg pairs, and using the previously obtained $\gamma_{ij}(0)$ values. This has been done by assuming a linear addition of the contribution of the two distribution as,

$$\gamma_{\text{Tot}}^{r_{\text{CuCu}}}(r) = \gamma_{\text{CuCu}}^{D1}(0) \gamma_{\text{CuCu}}^{D1}(r) + \gamma_{\text{CuCu}}^{D2}(0) \gamma_{\text{CuCu}}^{D2}(r)$$

$$\gamma_{\text{Tot}}^{r_{\text{MgMg}}}(r) = \gamma_{\text{MgMg}}^{D1}(0) \gamma_{\text{MgMg}}^{D1}(r) + \gamma_{\text{MgMg}}^{D2}(0) \gamma_{\text{MgMg}}^{D2}(r)$$

$$\gamma_{\text{Tot}}^{r_{\text{CuMg}}}(r) = \gamma_{\text{CuMg}}^{D1}(0) \gamma_{\text{CuMg}}^{D1}(r) + \gamma_{\text{CuMg}}^{D2}(0) \gamma_{\text{CuMg}}^{D2}(r)$$

(D.4)

Where each population has considered to have a log-normal distribution as,

$$\gamma_{\text{To}}^{D(k)}(r) = \int_{0}^{\infty} \gamma_{\text{To}}^{D(k)}(r,R) f(R) dR$$

(D.5)

Where $\gamma_{\text{To}}^{D(k)}$ is given by Eq. 5.3 and $f(R)$ is defined as,

$$f(R) = \frac{1}{(2\pi)^{1/2} \sigma R} \exp\left\{-\frac{1}{2} \left(\frac{\ln(R/R_m)}{\sigma}\right)^2\right\}$$

(D.6)

From this general strategy, the median radius and the with of the two proposed distributions, can be obtained.
Appendix E

Results of Al-Mg-Cu Alloy Pre-Deformed Material During Aging at 160 °C

In this appendix the resistivity and mechanical strength results, pertaining to the Al-3.23 at.% - 0.23 at.%Cu system processed as in Chapter 6, and aged 160°C, will be shown.

The resistivity results for material with previous deformation are shown in Fig. E.1, these plotted alongside the aging response of the material starting from the as-solutionized state (figure E.1). As already noted for the as-solutionized case, the aging times investigated were not sufficient to see the expected drop in resistivity at long times. Rather, one sees that all three conditions reach approximately the same level of resistivity and remain nearly constant for the full length of aging, this being consistent with the behaviour shown above for 200°C at times < 100 min (Fig. 6.2).

![Figure E.1: Resistivity evolution of Al-3.23 at.% - 0.23 at.%Cu alloy, artificially aged at 160 °C.](image)
Figure E.2 shows the yield stress evolution of the pre-deformed material along with material where not level of level of pre-deformation has been applied. The results are analogous to the material artificially aged at 200°C (Fig. 6.4), namely, for material pre-deformed 44 MPa, the magnitude of the rapid hardening effect is significantly lower than in material with no pre-deformation, measured from the as-deformed value, while for the case of material pre-deformed 174 MPa, a quick drop in yield stress after the first 2 minutes of artificial aging can be observed. As in the case of material artificially aged at 200 °C, the yield stress evolution, during artificial aging, is plotted with parallel dashed lines for each of the aging curves, the slope of these lines have been taken from the best fit to the as-solutionized material’s aging response. This reveals that, despite the applied levels of pre-deformation, similar kinetics control the strengthening during aging.

**Figure E.2:** Yield stress evolution of Al-3.23 at.% - 0.23 at.%Cu alloy, artificially aged at 160 °C.
Appendix F

Mechanical Analysis of Al-Mg-Cu System: Complementary Results

In this Appendix, the comparison between the experimentally obtained evolution of pre-deformed material compared to the modeled ones will be shown. The first section shows the.

F.1 AA5252 alloy results

In this section results from the AA5252 alloy subjected to pre-deformation and later artificially aged will be shown
Figure F.1: Experimental and modeled Kocks-Mecking representation of AA5252 (Al-2.94 at.% Mg) system, pre-deformed $\Delta \sigma = 44$ MPa, during artificial aging at 160 °C.
Figure F.2: Experimental and modeled Kocks-Mecking representation of AA5252 (Al-2.94 at.% Mg) system, pre-deformed $\Delta \sigma = 44$ MPa, during artificial aging at 160 $^\circ$C.
Figure F.3: Experimental and modeled Kocks-Mecking representation of AA5252 (Al-2.94 at.% Mg) system, pre-deformed $\Delta \sigma = 44$ MPa, during artificial aging at 160 °C.
Figure F.4: Experimental and modeled Kocks-Mecking representation of AA5252 (Al-2.94 at.% Mg) system, pre-deformed $\Delta \sigma = 44 \text{ MPa}$, during artificial aging at $160 \degree \text{C}$. 
F.2  Al-3.23 at.% - 0.23 at.%Cu alloy results

In this section results from the Al-Mg-Cu alloys subjected to pre-deformation and later artificially aged will be shown.

Figure F.5: Experimental vs modeled Kocks-Mecking plots resulting from the stress vs. strain data for Al-3.23 at.% - 0.23 at.%Cu alloy deformed $\Delta\sigma = 44$ MPa ($\varepsilon = 2\%$), during artificial aging at 160 °C.
Figure F.6: Experimental vs modeled Kocks-Mecking plots resulting from the stress vs. strain data for Al-3.23 at.% - 0.23 at.%Cu alloy deformed $\Delta\sigma= 44$ MPa ($\varepsilon = 2\%$), during artificial aging at 200 °C.
Figure F.7: Experimental vs modeled Kocks-Mecking plots resulting from the stress vs. strain data for Al-3.23 at.% - 0.23 at.%Cu alloy deformed $\Delta\sigma = 174$ MPa ($\epsilon = 10\%$), during artificial aging at 160 °C.
Figure F.8: Experimental vs modeled Kocks-Mecking plots resulting from the stress vs. strain data for Al-3.23 at.% - 0.23 at.%Cu alloy deformed $\Delta \sigma = 174$ MPa ($\varepsilon = 10\%$), during artificial aging at 200 ºC.