

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

TMT4905 -master thesis

The effect of cooling rate from solution heat treatment on ductility in Al-Mg-Si crash box alloys

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Abstract

The effect of cooling rate from solution heat treatment of Al-Mg-Si alloys on ductility has been investigated. Three different alloys were cooled with four different cooling methods, cold water, boiled water, air with convection, and still air. Strength and ductility was evaluated in relation to each other by tensile and bending testing. The 6063 alloy was characterized with stereo microscope, optical microscope and TEM. All the tested alloys showed significantly better bendability when cooled in cold water compared to boiled water while the strength was approximately the same. The alloys low in Mn content displayed the highest fracture strain in the fastest cooled condition.

The fastest cooled condition of the 6063 alloy showed a larger fracture strain, higher bendability and more significant area reduction of fracture surface than the condition with the second most rapid cooling. The material cooled in cold water was found to have a narrower PFZ around grain boundary, lower precipitate density and lower volume fraction of precipitates than the material cooled in boiled water. It is suggested that a narrow PFZ reduces strain localisation in proximity to grain boundaries and thereby increases ductility. The proposed mechanism depends on the fracture mode which is not analyzed in this work.

Sammendrag

Effekten på duktilitet av kjølehastighet fra innherding av Al-Mg-Si-legeringer er undersøkt. Tre forskjellige legeringer ble avkjølt med fire forskjellige kjølemetoder. Disse var kaldt vann, kokt vann, luft med konveksjon fra vite og stille luft. Styrke og duktilitet ble evaluert i forhold til hverandre ved strekk- og bøyetesting. 6063legeringen ble videre karakterisert med stereomikroskop, optisk mikroskop og TEM.Alle de testede legeringene viste signifikant bedre bøylighet ved avkjøling i kaldt vann sammenlignet med kokt vann. Styrken var omtrent den samme. Legeringene med lavt Mn-innhold viste den høyeste bruddtøyningen i den raskeste avkjølte tilstanden i motsetning den med rikere innhold av Mn.

Den raskeste avkjølte tilstanden til 6063-legeringen viste en større bruddtøyning, høyere bøybarhet og mer signifikant reduksjon av bruddoverflaten enn den tilstanden med nest raskeste avkjøling. Materialet som ble avkjølt i kaldt vann viste smalere PFZ rundt korngrense, lavere presipitat tetthet og lavere volumfraksjon av presipitater enn materialet avkjølt i kokt vann. Det foreslås at en smal PFZ reduserer lokalisering av tøyning i nærheten av korngrenser og dermed øker duktiliteten. Denne mekanismen avhenger av bruddmekanismen som ikke er analysert i dette arbeidet.

Preface

This master thesis was written during the final semester of the 5-year Materials Science and Engineering program at the University of Science and Technology (NTNU) in the spring of 2022. The thesis was conducted in collaboration with Benteler, SFI Physmet and TEM Gemini Centre and is a continuation of the project work done in the autumn semester of 2021. The results related to mechanical testing have been reused in this thesis. This work aims to explain why rapid cooling after extrusion (or solution heat treatment) can increase ductility in an aluminium crashbox. Differences on a nano- and microstructure level is expected to be present.

I want to thank my supervisor Knut Marthinsen and co. supervisor Randi Holmestad for excellent guidance and many insightful discussions related to physical metallurgy and TEM. I also want to thank my co. supervisors at Benteler, Yngve Langsrud and Lars Lodgaard, for giving me a warm welcome and thorough introduction to the aluminium and automotive industry. They used their refined metallurgical competence to create this well-designed project. My supervisors have all inspired me to pursue a professional career in the aluminium industry, starting this fall. Many hours have been spent in the lab, especially in front of the TEM. I would not have succeeded in obtaining the results if it had not been for Emil Frang Chrstiansen and Bjørn Gunnar Soleim, giving me thorough training in operating the TEM and how to make thin specimens.

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Abbreviations

- AA Artificial Aging
- BF Bright Field
- CBED Convergent Beam Electron Diffraction
- DF Dark Field
- EDS Energy Dispersive Spectroscopy
- GP-zones Guinier-Preston-zones
- HRTEM High Resolution Transmission Electron Microscope
- NA Natural Aging
- OM Optical Microscopy
- PFZ Precipitate Free Zone
- SHT Solution Heat Treatment
- SSSS Supersaturated Solid Solution
- TEM Transmission Electron Microscope
- UTS Ultimate Tensile Strength

1 Introduction

Aluminium is a preferred material in the automotive industry due to its excellent properties, and its use is augmenting [1]. Due to its high strength-to-weight ratio, aluminium can replace steel or other heavier materials and save weight in veichles. By reducing the weight of cars, fuel consumption can be reduced and thus CO_2 emissions. Aluminium has massive potential for recycling and can thereby contribute to reducing environmental impact.

The material studied in this thesis is used in crash boxes which, together with the bumper beam, make up the bumper system. The role of the crash box is to absorb as much energy as possible to reduce the impact on the vehicle and passengers. A well-performing crash box should therefore be ductile. Ductility can be defined as a material's ability to sustain plastic deformation before fracture [2]. After a collision, A crash box performing perfectly would look like the bellows of an accordion that are pushed together.

The background and motivation for this project come directly from the automotive industry. The industry has observed that enhancements in ductility can be achieved by rapid cooling after solution heat treatment compared to somewhat slower cooling. This applies especially to certain 6xxx alloys, which are commonly used for extrusion. The extra ductility gained does not compromise with a lower strength which is often the case in metallurgy. The phenomenon is therefore viable for optimizing the properties of a crash box and similar materials used in other applications. This mechanism is not well understood on the micro-structure and nanoscale levels. It is the aim of this thesis to contribute to understanding this mechanism.

The studied alloys are all 6xxx alloys frequently used in the automotive industry. The alloys have good extrudability and can be processed to have excellent mechanical properties. Mechanical tests have been performed to obtain the mechanical performance. Further characterization was done by transmission electron microscopy, where needle-like particles called precipitates and grain boundaries were studied.

2 Theory

2.1 Mechanical properties of Aluminium

2.1.1 Al-Mg-Si alloys

Pure aluminium has low strength and is relatively soft. Therefore alloying elements are added to aluminium to increase its strength through particle hardening and solid solution strength mechanisms. Aluminium alloys are often divided into two main groups, cast alloys and wrought alloys and two sub-groups heat treatable and nonheat treatable. Cast alloys are usually more prone to deformation than Wrought alloys. All cast alloys obtain strength from solid solution strengthening, and some alloys can also be heat treated to form hardening precipitates. Heat-treatable alloys are alloys in which precipitate hardening is possible. Wrought alloys are designed for forming and deformation in the processing of the material and are therefore more ductile and have less resistance to deformation than cast alloys. Wrought alloys often have a smaller percentage of alloying elements to make them malleable. When wrought alloys are deformed at lower temperatures, they are hardened and achieve higher strength. In addition, heat treatable wrought alloys obtain higher strength by precipitation hardening which by far is the most important strengthening mechanism in the alloys. [3].

The 6xxx series of aluminium alloys have two main alloying elements, magnesium and silicon, typically with a content of 0.5-1.3 wt% and 0.4-1.4wt%, respectively. These alloys can be both heat-treated and wrought to achieve higher strength. Secondary alloying elements such as manganese, chromium and copper are often added. Mn and Cr have a grain refining effect, while Cu enhances the alloy's strength by precipitation but makes it more exposed to corrosion. Because of its properties, the 6xxx series are the most frequently used alloys for extruded aluminium profiles. The $R_p 0.2$ strength of this series is typically in the range of 190-360 MPa [3].

2.1.2 Dislocations

Dislocations are important for the deformation behaviour and strength of metals. Deformation takes place by movement of dislocations. Dislocations are linear defects in the crystal lattice where some atoms are misaligned. A dislocation is defined by its direction and displacement. The direction of a dislocation at a certain point is given by its line vector, \vec{t} . The Burgers vector, \vec{b} , describes the magnitude and

direction of the slip in the lattice [4]. There are two main types of dislocations, screw and edge, while most are a combination of the two. In an edge dislocation, an extra half-plane of atoms is inserted in the lattice, so the \vec{b} is perpendicular to the dislocation line. As a consequence of the extra inserted plane, the atoms just above the dislocation line are squeezed together. Below the end of the extra halfplane, the atoms are pulled away from each other. The strain zones are illustrated in Figure 2.1. Dislocations of screw character have \vec{b} parallel to the dislocation line.



Figure 2.1: An edge dislocation showing with marked zones of tension (yellow) and compression (green) [2].

The shear stress required for a theoretical slip of a crystal is many times higher than the observed stress from experiments which can be attributed to the movement of dislocations. The stress needed to move a dislocation step by step, as shown in Figure 2.2, is close to the experimentally observed stress for slip. Dislocations can move by two main types of motion. The most common is a glide, a movement within a slip system defined by a slip plane and slip direction. The second type of motion is called climb and occurs when a dislocation moves out of its glide plane and normal to the Burgers vector before it continues to glide in a slip system [5].



Figure 2.2: Movement of an edge dislocation where arrows represent the shear stress[5].

2.1.3 Strengthening mechanisms

Perfect single crystals do not exist in metals on a macroscopic scale. Defects are introduced to metals during solidification, thermal processing, deformation and forming processes. Strengthening mechanisms are based on defects in the crystal of the metal lattice and their ability to hinder the movement of dislocations. The most important for aluminium alloys are presented in this section.

Solid solution strengthening

Solid solution strengthening occurs when atoms of elements of a different size than the base metal atoms are introduced to a crystal lattice. The foreign atoms can be placed substitutionally or interstitially in the crystal lattice, depending on the size difference. Strains in the lattice are imposed on the surrounding atoms and counteract dislocation movement. As a result, metals containing alloying elements are stronger than pure metals [2]

Strain hardening

The phenomenon where the stress required to cause slip increases as a result of previous plastic deformation is called strain hardening. The contribution to an alloy's strength from dislocations is described by equation Equation 1 where τ is the flow stress and ρ^T is the total density of dislocations. τ_0 includes stress from other strengthening mechanisms, G is the shear modulus, b is the length of the Burgers vector and C is a constant[6].

$$\tau = \tau_0 + \alpha G b \sqrt{\rho^T} \tag{1}$$

When a metal is plastically deformed, dislocations first move until immobile and are then stored in the matrix. The number of dislocations can multiply during plastic deformation. The dislocations form a complex network and interact with each other, impeding the movement of other dislocations. Strain hardening will therefore increase with the density of dislocations which is referred to as work hardening [4]. The cost of an increase in strength is often a gradual reduction of ductility in the material [2]. Aluminum has a face-centered cubic structure (FCC) and can slip in the four $\{111\}$ -planes and in the three < 110 > directions. This sums up to twelve combinations, i.e. aluminium has 12 slip systems that define where dislocations can exist and move [5].

Hardening by grain boundaries

The grain size of polycrystalline materials contributes to strength i.e. hinders dislocation movement. When a dislocation moves and meets a grain boundary, the dislocation will most likely be stored there or reflected. Due to the crystallographic orientation differences between grains, the dislocation faces discontinuation in its glide plane. As a result, dislocations tend to pile up at grain boundaries. The shear stress in front of a boundary increases with the number of dislocations in the pile-up. If the shear stress becomes large enough, dislocations can slip across the grain boundary. This is more plausible in a large grain where more dislocations are accessible to pile up than in a small grain [7]. The Hall-Petch equation, Equation 2, describes the relationship between grain size and yield strength, y_0 . The strengthening contributions from other strengthening mechanisms is σ_0 , k_y is a material constant, and d is the diameter of the grain [2].

$$\sigma_y = \sigma_0 + k_y \sqrt{d} \tag{2}$$

Precipitation hardening

In precipitation hardening, a dispersion of particles is precipitated in the matrix and impedes the movement of dislocations. If the particles are non-shearable, i.e., strong enough to withstand the force from the dislocations, the dislocation is first pinned by the precipitates as seen in Figure 2.3 [8]. As the dislocation movement continues to the right, it will loop around the precipitates and form Orowan loops [4]. Stress fields around the precipitates are increased from the loops and work against dislocation movement.



Figure 2.3: Non-shearable precipitates pinning a dislocation (a), formation of Orowan loops (b) and (c) [8].

If the precipitates are shearable, i.e., not strong enough to withstand the stress from the line tension of the dislocation, they are instead cut as depicted in (b) and (d) Figure 2.4. Cutting costs more energy for the dislocation rather than moving through the matrix. After shear of a particle the the slip plane is softened and further slip has a tendency to occur in the same plane. In the opposite case, Orowan loops makes it more difficult to slip in the same plane thus making the slip more homogeneous. Precipitates that are small and coherent are often shearable. As the aging process (to be discussed in later sections) progresses, the precipitates are more likely to become non-shearable [9].



Figure 2.4: Sheared particles (b) leads to slip accumulations, while non-shearable particles (c) leads to relative homogeneous slip (e)[8].

2.1.4 Nucleation

Phase transformations in solids start with the nucleation of a new phase. Consider a two-component system of A and B where β -phase rich in B precipitates in α -phase supersaturated with B. Before Nucleation of β can commence, enough B atoms must diffuse into a small confined volume to achieve the composition of β . The atoms can then rearrange into the crystal structure of β to form a nucleus creating an interface between the two phases with associated surface energy, γ , and area, A. The surface gives a free energy increase of $A\gamma$ while the created volume of β gives a negative contribution to the free energy equal to $V\Delta G_V$. The lattice structure of the nucleus will likely have a mismatch with the lattice of the matrix. This gives rise to a strain misfit energy, ΔG_S , which is proportional to the nucleus's volume and increases the free energy. The free energy related to formation of a β nucleus, ΔG , is summed up by Equation 3 [10].

$$\Delta G = \gamma A - V G_V + \Delta G_S \tag{3}$$

Considering nucleation of a sphere with radius, r, the free energy of the surface area is proportional to r in the power of two and the power of three for the volume term. Therefore the free energy increases with the size of the nucleus until it reaches a max at the critical point, r^* and ΔG^* shown in Figure 2.5. At this point, the free energy decrease with a further increase in r, which means ΔG^* acts as an energy barrier. If the energy barrier is overcome, the nucleus is dramatically more stable [2].



Figure 2.5: ΔG as a function of nucleus radius and showing the activation energy barrier ΔG^* [10].

The shape of a sphere gives the lowest surface area possible for a given volume, resulting in a high energy barrier for nucleation and is called homogeneous nucleation. Considering an interface between solids γ will vary significantly according to the degree of coherency. An Incoherent interface gives a high value of γ thus lessening the energy barrier for nucleation, while a coherent interface gives a low value. Nucleation is most likely to happen heterogeneously on a nucleation site to decrease the interface area between matrix and particle and thus reduce the free energy from the surface. Possible nucleation sites are listed below, from most favorable sites to least [10].

- Free surfaces
- Grain boundaries
- Stacking faults
- dislocations
- Vacancies
- homogeneous sites

2.2 Process-route

In this section the processes in the production of aluminium profiles that is used to make the material investigated in this thesis is covered.



Figure 2.6: The process route as a sequence from casting to age hardened profile. Printed with permission from Benteler.

2.2.1 Direct chill continuous casting

The casting process begins by melting the charge material, consisting of high purity aluminium ingot, processed in-house scrap, and alloying elements. The alloying elements with a low melting point are added to the aluminium as pure metal bars, while those with a high melting point are added as master alloy bars. Master alloys are made separately by melting different alloying elements with aluminium to reduce the melting point. In the direct chill continuous casting process, molten aluminium is poured into a shallow mould with a circular cross-section and water-cooling. The false bottom of the mould is lowered at a controlled rate as the molten aluminium solidifies. Water is sprayed on the billet just after solidification to increase the cooling rate [11].

In the casting of aluminium billets, a fine equiaxed grain structure is desired for better mechanical properties of the final product. The final grain size is a result of several factors. The most influential are alloy composition, solidification rate, and addition of grain refiners. The grain refiners work by introducing sites energetically favored for nucleation of aluminium; thus, a higher number of grains are formed, reducing the grain size. An effective grain refiner minimizes the risk of hot cracking, hydrogen porosity, and shrinkage. A master alloy of Boron, titanium and aluminum is widely used as grain refiner [11].

The distribution of alloy elements in a solid phase will differ from the melt's uniform concentration before solidification. The redistribution of alloying elements is a phenomenon called segregation and results from the alloying elements having a higher solubility in molten aluminium than in solid aluminium. Local equilibrium between two phases will result in concentration differences to satisfy thermodynamic requirements. Areas where the metal melted last will have a higher concentration of alloying elements. Local concentration gradients in the size range of single grains are called microsegregation and will be present in all cast products to a certain degree [12]. Concentration differences depend on the alloy's solubilities given by the phase diagram, and solidification rate [13]. Macrosegregation can also occur and is where concentration differences appear on a much larger length scale and is considered a casting defect. It is found in larger cast products where some of the metals solidify later than other parts and therefore have a higher concentration, and can also be caused by relative movement between the liquid and solid phase [14].

2.2.2 Homogenisation

Cast billets are homogenized before extrusion to enhance quality and workability. This is performed in three steps heating the billet at a controlled rate, holding a certain temperature for a specific amount of time, and cooling the billet at a sufficient rate. Alloying elements diffuse from grain boundaries and other regions rich in solute towards grain centers [13]. The diffusion is augmented at elevated temperatures, decreasing the concentration gradients in the billet over time. Microsegregation can be eliminated with homogenization, while the distances in macrosegregation are too large to be appreciably affected by homogenization [14].

The time required to obtain homogeneity is dependent on homogenization temperature, diffusion distances, i.e., grain size, and diffusion coefficients of the alloying elements. The temperature should never surpass the lowest melting point of the present phases of the particular alloy as this will lead to local melting [15]. Too high temperatures can damage the microstructure such as segregation, voids and blistering [11]. Homogenization serves the role of precipitating and distributing intermetallic compounds called dispersoids, which are particularly important for highstrength alloys. The dispersoids are precipitated homogeneously on the surface of other precipitated particles, which redissolve later while the dispersoids remain [13]. A uniform distribution of dispersoids is essential to have control of grain structure evolvement in subsequent heat treatment, which is described in the section about dispersoids. A fine distribution is achieved by having a relatively slow heating rate (around 75°C/h) and selecting an appropriate homogenizing temperature.

2.2.3 Direct extrusion

Extrusion offers a relatively cost-effective method of manufacturing aluminium products with complex shapes as long profiles. Extruded aluminium products are encountered in everyday life in automotive vehicles, window and door frames, roofing, furniture, rail vehicles and other applications. About 90% of the extruded aluminium profiles are 6xxx alloys [16].



Figure 2.7: Schematic illustration of a direct extrusion press [11].

Direct Extrusion is the most commonly used extrusion method where a billet is placed in a container and pushed through a die by a hydraulic pressured ram as illustrated in Figure 2.7. The ram stem pushes with a force that is countered by friction forces from the die and the container walls, as shown in figure Figure 2.8. The metal flows in the same direction as the ram moves. As mass from the billet is extruded, the end of the billet comes closer to the die and the friction between the container wall and the billet is reduced. This is the basis for the characteristic curve for ram stem pressure vs. the ram position [11].



Figure 2.8: Stem force plotted VS. ram position [11].

Before starting the extrusion process, the die is preheated to a temperature that is about the same as the aluminium meeting the die, 500-550°C. First, the ram pushes the billet which has a slightly smaller diameter than the container, towards the die. The container and die are filled with metal before the profile starts to be extruded. At this point, the stem force will reach its peak and continuously decrease until the ram reaches its stop position. In what is referred to as billet on billet extrusion, the container moves to the butt of the first billet and is cut off before a new billet enters the press. The butt is removed as it contains "billet skin contamination" due to the DC casting process and has a different microstructure. The contamination has a different chemical composition, including oxides, dirt, and impurities. The skin layer of the billet is pushed away from the die by the friction forces from the container [17].

Contamination accumulates at the end of the billet. The length of the butt cut-off is dimensioned to ensure that a sufficiently low amount of the skin layer flows into the mass that will be extruded. The container is moved back into place, and a new billet can start to be pushed towards the die by the ram. The remainder of the last billet and the front of the new billet will form a charge weld. Usually, the front and the back of a profile with proximity to the charge weld are cut off and scrapped. Therefore, contamination inflow from the skin layer around the charge weld can be tolerated [17].

2.3 Age hardening

Several mechanisms give increased strength to metal and include strengthening by grain boundaries, solid solution strengthening, and deformation. For heat treatable aluminium alloys, precipitation by age hardening significantly contributes to strength. Age hardening is performed after extrusion and includes two heat treatments with controlled heating and cooling as shown in Figure 2.9. Solid solution heat treatment (SHT) is the first step of age hardening, but in some cases, the extrusion process can be used as SHT. The material is quenched before the subsequent heat treatment is performed, where precipitation hardening occurs.



Figure 2.9: Temperature vs time during SHT and AA, time for NA between SHT and AA is not added in this figure. [2]

2.3.1 Solid Solution heat treatment

Aluminium alloys typically have more than one stable phase at room temperature. During solid solution heat treatment, the alloy is heated to a temperature with a onephase region. This corresponds to temperature, T_0 , in Figure 2.10 and Figure 2.9. A requirement for the alloy to be heat treatable is a large enough increase in solubility of alloying element in the α -phase with increasing temperature. T_0 is held for the time required to dissolve all solute in the primary α -phase. Then the temperature is quenched to a temperature where diffusion is extremely slow. At T_1 , the Gibbs free energy of formation of β phase is below zero, and the reaction is thus spontaneous. However, the drop in temperature is fast enough to prevent diffusion and formation of β phase. The material has become a super saturated solid solution (SSSS) and can remain unstable for a long period of time at room temperature.



Figure 2.10: Binary phase diagram of a binary alloy where T_0 is the temperature at SHT, T_1 after quench and T_2 at AA [2].

2.3.2 Artificial aging

The next step in the age-hardening process is artificial aging (AA). The temperature is elevated from T_1 to T_2 , where the diffusion rate is augmented and still in a twophase region of the phase diagram. Finely dispersed particles of a second phase will then start to precipitate. As particles nucleate and grow as precipitates, the amount of solute is decreased, and so is solid-solution strengthening. A high enough number of nucleation sites are necessary to get finely dispersed precipitates which outweigh the reduction in strength from solid-solution strengthening. For some alloys, precipitation will also occur when left at room temperature after SHT, termed natural aging (NA) [13].

The driving force of a SSSS is to form the equilibrium phase, which in 6xxx alloys is named β with the chemical formula Mg_2Si . However, several different meta-stable phases of precipitates exist in the Al-Mg-Si system, and they form in a specific and complex sequence shown in Equation 4 [18].

$$SSSS \to Mg/Si \text{ clusters} \to GP\text{-zones} \to \beta'' \to \beta', U1, U2, B' \to \beta, Si$$
 (4)

When starting AA, the SSSS contains both a surplus of vacancies and excess solute. Vacancies are prerequisites for forming precipitates and the quantity of them increases with temperature [19]. Vacancies form clusters that attract solute atoms and thereby have catalyzing effect for nucleation [20]. After starting AA, atomic clusters of Mg, Si, or a combination of the two are formed [21]. Then the atomic clusters transform into Guinier Preston (GP) zones [18]. GP-zones are ordered groups of atoms rich in solute with a thickness of only a few atoms [13]. These groups of atoms form at this stage because they are fully coherent with the matrix and therefore have small surface energy, which promotes formation as discussed in the section about nucleation [10]. The matrix surrounding the GP-zone is subjected to elastic strains despite the coherency. GP-zones are sheared by dislocations and have a small effect on the impending movement of dislocations. A significant increase in yield strength is associated with the formation of GP-zones, which might be due to their high number density [13].

GP-zones are transformed further into β ". This transition phase has higher activation energy for nucleation than the GP-zones and lower than the equilibrium phase, β . The same principle applies for each step in Equation 4. Maximum achievable hardness (and thus strength) obtained from AA is often observed to occur at an aging time that results in a majority of β " precipitates [22]. These are needle-like precipitates that grow in [001] directions of the matrix. Further aging from the peak aged condition results in overaging and the formation of several particles are, B', β ' U1 and U2. The evolvement of strength during AA is illustrated with corresponding phases is shown in Figure 2.11. By aging further, the equilibrium phase β can form. Commercially a temperature around 150-190°C is used and is too low to form β .

The time between SHT and AA can significantly impact the alloys' response to AA. Pre-aging at 80°C and natural aging at room temperature prior to AA can increase peak hardness compared to starting AA directly after quenching from SHT [23]. The effect of pre-aging before AA is dependent on the amount of Mg and Si. Enhancement can be achieved for alloys with less than 0.9% Mg and Si. It has been

suggested that NA before AA can result in a bimodal distribution of precipitate size while no pre-aging gives monomodal distribution[22]. This can be explained by the impact of clustering vacancies and clustering during NA.



Figure 2.11: Strength plotted vs. the logarithm of time during AA with the present phases inscribed [24].

2.4 Particles in heat treatable Al-Mg-Si alloys

2.4.1 Dispersoids

Particles classified as dispersoids are formed in 6xxx-alloys when heating them to their homogenization temperature or while holding the temperature. These secondary phase particles are not directly considered strength contributors but yield positive effects for deformation behavior, and resistance to recrystallization [25]. Recrystallization and grain growth are retarded by the dispersoids quality of pinning grain boundaries.

The dispersoids size and distribution depend on the amounts of alloying elements, time and temperature of the homogenization process. The diameters are generally in the range of 10-500 nm. Relatively low homogenization temperatures and short times tend to favor smaller particles that are densely distributed. Increasing the time and temperature generally leads to coarser particles [13].

The chemical composition of dispersoids varies with the alloy. Disperosids in alloys containing Cr and /or Mn are referred to as α -Al(Mn-CrFe)Si [26] CrFe)Si precipitates. Depending on the Si concentration Al_6 (Mn,Fe) can be present and is promoted by a low Si concentration. Al_6 (Mn,Fe) can transform into α -Al(Mn-CrFe)Si by a eutectoid phase transformation [27].

2.4.2 PFZ- precipitate free zones

Heat-treatable alloys will have zones without precipitates, referred to as PFZs. These zones arise by two identified mechanisms, drainage of solute and drainage of vacancies reducing the potential for precipitation [28]. PFZs are typically found around grain boundaries and dispersoids and are shown in Figure 2.12. A grain boundary act as a sink for vacancies, except when the misorientation between grains is very small($\sim 2^{\circ}$) [29]. Precipitated particles can cause solute depletion in the surrounding area [30].

The PFZ depleted of solute and vacancies is much softer than the grain interior containing large amounts of precipitates. The soft zone can cause strain relaxation or a local strain accumulation during deformation. Large local strains in softer PFZ should stimulate to rise of microvoids formed at grain boundaries and promote fracture [31]. Ductility may be increased by the relaxation of a high concentration of stresses in front of slip bands which can impede the growth of microvoids at GB precipitates.

The importance of the width of PFZ has earlier been unclear [31] while newer studies have suggested complex yet significant relations. A correlation between narrower tensile fracture strains and wider PFZs has been found for Al-Zn-Mg alloys [32]. Studies have been performed on the quench sensitivity of Al-Mg-Si alloys, and some mechanisms have been suggested. A material susceptible to inter-granular failure can achieve better ductility with a wide PFZ obtained from slow cooling. While the ductility of a material not exposed to intergranular failure can be enhanced with a narrow PFZ [33].



Figure 2.12: TEM BF mages of PFZ's from the 6063 alloy of this thesis around a grain boundary (a) and surrounding a dispersoid (b).

2.5 Mechanical properties and testing

2.5.1 Tensile testing

The uniaxial tensile test is often used to acquire essential information on the mechanical properties of materials. In a tensile test, a specimen is subjected to a uniaxial force parallel to the direction of its length. The applied force causes the elongation of the specimen. The elongation and applied force are logged and plotted against each other to obtain a characteristic stress-strain curve shown in Figure 2.13. The engineering stress, σ , and engineering strain, ϵ , can be calculated from Equation 5 and Equation 6 respectively. F is the force applied, A_0 is the initial cross-section, ΔL is the elongation and L_0 is the initial length. When calculating engineering stress, the cross-section area of the specimen is considered constant for all strains, while in reality, it decreases with increasing strength until fracture [2].

$$\sigma = \frac{F}{A_0} \tag{5}$$

$$\epsilon = \frac{\Delta L}{L_0} \tag{6}$$



Figure 2.13: Engineering stress-strain curve [4]

Irreversible deformation is introduced when the stress applied exceeds what can be elastically deformed and the relation between stress and strain is no longer linear. A linear relation between stress and strain exits for minor strains and is called the Emodulus. The strain following this relation is elastic, meaning that by releasing the force, the specimen will return to its original shape without any permanent deformation. The point where elastic behavior ceases is often defined as where a line with a slope equal to E-modulus starting at 0.2% strain intersects the stress-strain curve. The stress at this point is called 0.2% offset yield strength. By further increasing the stress from this point, dislocations are introduced to the crystal lattice, which makes the metal stronger, this is called strain hardening. At first, strain hardening more than compensates for the reduction in cross-section, so the engineering stress continues to increase. A maximum applied load occurs at the point where the change of cross-section area equals the effect of strain hardening and is called the ultimate tensile strength. At this point, necking starts and involves a local constriction in the cross-section where further plastic deformation of the specimen is concentrated in this area. The applied load decreases with further strain until fracture of the specimen [4].

There are two commonly used measures of ductility obtainable from a tensile test. The elongation at fracture, ϵ_f , which occur at the specimen length, L_f is calculated from Equation 7. The second one is the relative reduction of the cross-section area at fracture, q, is given in Equation 8 where A_F is the cross-section area at fracture.

$$\epsilon_f = \frac{L_f - L_0}{L_0} \tag{7}$$

$$q = \frac{A_0 - A_f}{A_0} \tag{8}$$

2.6 Electron microscopy

Electron microscopy is an important tool for material characterization on the nanoscale. It is in many aspects similar to light microscopy as operation and physics behind it are analogous. Where a light microscope bends photons in visible light with glass lenses, an electron microscope uses electromagnetic lenses to bend electrons. An electron microscope can vary the power of its electromagnetic lenses with fixed positions, whereas a light microscope has lenses with fixed powers and adjustable positions. A photon has a wavelength that depends on its energy. This is also the case for electrons when considering them as waves. The wavelength, λ , can be calculated from Equation 9 where h is the Planck constant, m_0 is the mass of the electron, e is the charge of an electron and V is the accelerating voltage, and c is the speed of light in vacuum. Applying an accelerating voltage of 200kV gives $\lambda=0.0251$ Å [34].

$$\lambda = \frac{h}{\sqrt{2m_o eV(1 + \frac{eV}{2m_0c^2})}}\tag{9}$$

For a visible light microscope the Rayleigh criterion, Equation 10, is used to approximate the smallest resolvable distance, δ . Further μ , β and λ are the refractive index, semi-angle of the magnifying lens and the wavelength of photons, respectively [34]. Considering blue light with a wavelength of 450 nm and the numerical aperture $(\mu \sin \beta)$ equal to unity would give a resolution of 275 nm.

$$\delta = \frac{0.61\lambda}{\mu \sin(\beta)} \tag{10}$$

There is a similar relationship to approximate the best resolution in TEMs, Equation 11. As the wavelength of electrons are several magnitudes smaller for electrons than visible light, it becomes clear that a drastically higher resolution is achievable with electron microscopy [34].

$$\delta = \frac{1.22\lambda}{\beta} \tag{11}$$

2.6.1 Electron interactions

A beam of high-energy electrons moving towards a thin specimen will result in several interactions between the electrons and specimen material as shown in Figure 2.14. Many of these interactions produce signals that can be detected using electron microscopy techniques and are used for imaging.

Electrons in the incident beam can pass through the specimen unaffected and continue in the direct beam. However, some electrons interact with the specimen's crystal lattice, which alters their direction, energy, or both. The electrons affected by the specimen are referred to as scattered electrons. Scattering with energy loss is called inelastic scattering and elastically scattered electrons have conserved energy. Scattered electrons can be separated into coherent and incoherent. Coherent electron waves are in phase (step) with one another as opposed to incoherent electrons, where there is no phase relationship of the waves after interacting with the specimen. Additionally, scattered electrons are classified as forward scattered if the scattering angle is less than 90° and back scattered if it is larger than 90°.



Figure 2.14: Electron signals from a high-voltage electron beam [34]

2.6.2 Electron diffraction

Atoms are arranged systematically in crystals, leading to destructive and constructive interference from scattered electrons. When an incident beam of coherent electrons is scattered elastically, a reciprocal relationship between scattering angles and atomic plane distances is given in Bragg's law, Equation 12. When two electron waves diffract at two different points with the same angle, θ , the difference in traveled path equals an integral number, n, of wavelengths λ . The phenomenon is illustrated in Figure 2.15. As a result, the interplanar lattice spacing, d, in an area of a crystalline specimen can be determined, the acceleration voltage is user-controlled, so the electron energy is known, and thus , θ are measured experimentally.

$$2d_{hkl}\sin(\theta) = n\lambda \tag{12}$$



Figure 2.15: Bragg diffraction of an electron beam [34].

2.6.3 Transmission electron microscopy

In transmission electron microscopy (TEM), an electron gun emits high-energy electrons, which pass through a sample and a series of magnetic lenses. The electrons produce signals which are registered and used in various TEM techniques. The microscope has three central systems, the illumination system, and the projecting system. The placement of the essential components, apertures, and lenses in a TEM can be seen in Figure 2.16.



Figure 2.16: A schematic drawing of a TEM [35]

The illuminations system comprises the electron gun, Several condenser lenses and a condenser aperture. The function of the condenser aperture is to control the size of the specimen's area illuminated by a parallel beam. Thereby one can omit electrons emitted from higher angles. The role of the condenser lenses is to control the size of the beam. A parallel beam (wide) or a convergent beam (narrow) are the two principal modes of operation.

Two types of electron guns are used in TEMs: thermionic and field-emission (FEG). Modern TEMs with a thermionic electron source use a LaB_6 -crystal. A metal wire is bonded to the crystal and is heated from resistance by applying a large voltage which causes thermionic emission of an electron current from the cathode. The field emission gun uses a large difference in electric potential to create an electron current. The FEGs tip work as a cathode with respect to the two anodes. The first anode is positively charged, extracts electrons and pulls them out of the tip, and the second anode accelerates the electrons to a specific voltage. A FEG has a narrow tip that can produce a higher current density for a small area than a thermionic gun which can provide a higher current density for large areas. A FEG also produces a more coherent beam than a thermionic electron source [34].

The imaging system comprises the crucial objective lens and two objective apertures. The objective aperture is used to select electrons that have scattered at particular angles. A confined space of about 10mm in the length of the column includes the specimen stage system and objective lens. This is where all-electron- specimen interaction takes place and thus where images and diffraction patterns originate. Image contrast and resolution are especially dependent on the performance of the objective lens.

The imaging system consists of several lenses situated below the objective lens. Intermediate and diffraction lenses magnify an image or diffraction pattern. Finally, a projector lens focuses a final diffraction pattern or image of a specimen onto a viewing screen or camera.

2.6.4 TEM operation modes

A wide range of modes and techniques exist for TEM. The ones used for this thesis are included in this section.

Bright field and dark field imaging

Bright field (BF) imaging is perhaps the most common method for imaging materials in TEM. The objective lens focuses the transmitted electron beam from the specimen

to the back focal point. The beam will continue onto the image plane, where a point in the specimen will correspond to the same point in the image plane. A magnified image can be seen on the viewing screen or camera after the image has passed the projector lens. In the case where all electron beams are focused on the viewing screen, little contrast is given to the image. A BF-image is formed by inserting the objective aperture, which excludes scattered electrons as shown in Figure 2.18, giving the image more contrast. The contrast descends from different areas diffracting different amounts of electrons. Areas that appear dark in a BF image diffract many electrons. A reduction in the size of the objective aperture will increase contrast further. A dark field (DF) image is formed by only letting certain scattered electron beams pass the objective aperture. When inspecting a small area with a parallel beam, a selected area aperture can be inserted to block out scattered electrons from outside the area of interest.



Figure 2.17: Bright field and and dark field imaging [36]

HRTEM

HRTEM (high-resolution TEM) is a microscopy technique using phase-contrast as its main mechanism of contrast. It can be regarded as a type of Bright field imaging at a high resolution where both scattered beams and transmitted beams contribute to creating an interference image. Considering an extreme resolution in terms of Å and lattice parameters, diffracted electron waves will have extremely small angles between them as they go through the same point in the image plane. This results in the beam beginning to interfere with itself. Depending on how far from the optical axis the electrons are scattered, their traveled distance will differ accordingly, introducing phase shifts between beams. In addition, aberrations exist in the objective lens, which further disturbs the phases. Therefore the HRTEM applies aberration corrections. The technique can be used to inspect precipitates on grain boundaries, dislocations, surface structures, and more.

Diffraction mode

The objective lens focuses on beams scattered or diffracted with the same angles from the specimen to the same point in the back focal plane, regardless of where the beam passed the specimen. The same electrons are used to form a diffraction pattern or an image, but the intermediate lens's focus determines which can be seen on the viewing screen [37]. By altering the strength of the intermediate lens, one can switch between reciprocal space (diffraction pattern) and real space (image mode). A selected area aperture is inserted into the image plane above the intermediate lens and defines the area from which the diffraction is obtained, as shown Figure 2.18. This technique is called SAED (selected area diffraction). A parallel beam in SAED gives several spots on the viewing screen where each spot corresponds to a certain Bragg angle in Equation 12 [34].



Figure 2.18: Diffraction mode (a) and image mode (b) [37]

CBED and kikuchi patterns

The CBED(convergent beam electron diffraction) technique uses a convergent beam meaning the beam will be shaped like a cone in three-dimensional space with a tip of 1-100 nm. This means that the specimen will have incoming electrons from a larger range of angles as compared to SAD. Several sets of lattice planes will

then have Bragg scattering simultaneously [38]. There are numerous applications of CBED, including crystal orientation determination, local specimen thickness, lattice parameter measurements and crystal structure determination. The two former are used in this thesis.

Kikuchi patterns form when a convergent beam is transmitted through a crystalline specimen with a certain thickness. Two scattering events must occur to form Kikuchi lines [39]. A large number of electrons are forward scattered incoherently, and there must be domination of elastically scattered electrons rather than inelastic to form Kikuchi lines. These electrons are referred to as diffusely scattered and are subsequently Bragg diffracted by crystal planes in the specimen [34]. Kikuchi lines appear as pairs and correspond to Bragg angles where one is θ_B and the other $-\theta_B$. Due to the low values of θ_B the lines are approximately straight. The pair of Kikuchi lines form a Kikuchi-band with a width of $2\theta_B$ [40].

Zone axis refers to an orientation of high symmetry in a crystal or more specifically a direction along the intersection of crystallographic planes. FCC crystals have a four-fold symmetry in (001)-planes. This orientation of the crystal lattice, [001], is therefore recognizable with a four-fold symmetry in the HOLZ-reflection of a DP taken with CBED as shown in Figure 2.19.



Figure 2.19: CBED images of Zone axis (a) and Kikuchi band (b) from the 6063 alloy of used in this thesis.

EDS- energy dispersive spectroscopy

When an incident beam of electrons meets the specimen, it can cause emission of X-rays, which can be used for analysis of the chemical composition in the specimen. When the electron incident beam hits an atom in the specimen, it may enter an

excited state with higher energy. This happens if the atom can absorb the amount of energy corresponding to the discrete energy difference between having all electrons in the ground state and the state of having ejected an electron to an outer shell. When the atom returns to its ground state, a photon will be emitted with the energy difference between the two involved shells. As different elements have distinct energy differences between their shells, characteristic photons with energy in the range of X-rays are emitted for each element. The wavelength, λ , of the characteristic X-ray can be calculated from Moseley's law, Equation 13, where Z is the atomic number, and σ and K are constants related to which electron shells are involved [41].

$$\lambda = \frac{K}{(Z - \sigma)^2} \tag{13}$$

3 Experimental

This chapter describes the thermomechanical processing of the material used in this thesis, mechanical testing performed, optical light microscopy, preparation of TEM specimens, and methods used to obtain quantitative precipitate results from TEM analysis. Tensile testing, bending tests, and heat treatments were performed at SINTEF manufacturing Raufoss in August 2021. All further characterization and analysis were performed at NTNU Gløshaugen. Benteler automotive Raufoss provided the material used in this thesis. The three alloys have been mechanically tested, while only the 6063 alloy has been analyzed with TEM.

This thesis is a continuation of the project work from TMT 4500 carried out in the autumn semester of 2021. All experiments, specimen preparation, and analysis related to TEM have been carried out for this thesis only. Results from the mechanical tests from the project are included here as they provide essential information for this thesis.

3.1 Material

Material from three aluminium alloys provided for this thesis was extruded as squareshaped hollow profiles at Benteler Automotive Raufoss. The composition of the alloys is presented in Table 3.1. Specimens were machined from extruded profiles and used for all mechanical testing and material characterization. Twelve tensile and twelve bending test specimens were prepared for each of the three alloys by machining them from the sidewalls of extruded profiles.

Table 3.1: This table shows the alloying composition of the material provided by Benteler, all numbers are in in $\rm wt\%$

Alloy —	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr
6063	0.53	0.2	0.01	0.01	0.48	0.01	0.03	0.02	0
6005	0.72	0.2	0.02	0.14	0.53	0.01	0.03	0.02	0
6106	0.54	0.16	0.15	0.05	0.64	0.01	0.03	0.02	0

3.2 Thermomechanical Treatment

The material for a crash box goes through multiple thermomechanical steps before ending up as a finished product. First, aluminium alloys were cast as cylindrical billets with geometries fitted to the extrusion press and cooled. Then the billet was
homogenized by heating it and keeping it at a stable temperature of 575°C for 3 hours before being cooled at a controlled rate.

Before extrusion, the billet was preheated by induction. The temperature in the billet rises during the extrusion process. Due to heat generation from large friction forces between the extrusion die and the billet and also between the walls of the extrusion container and the billet, heat will accumulate during the extrusion of a billet. If a billet were to have a constant temperature throughout its length dimension before entering the extrusion press, it would result in the last part of the billet having a higher temperature than the first part when meeting the die. Therefore, the billet is heated more in the front than in the back. This temper enables keeping a stable temperature throughout the extrusion process. A hydraulic press extruded the billet to a long profile, pushing the billet through a die. The profile is then stretched ~ 1% by a puller before it is cut into smaller lengths and ready for SHT.

3.2.1 Solution Heat Treatment, Cooling and Aging

Four different cooling methods from solution heat treatment were conducted for each alloy. Three bending test specimens and three tensile test specimens from each alloy were put in a basket made of a thin metal lattice. Additionally, thermocouples were inserted into one tensile specimen and one bending specimen. The two specimens measured the temperature and were put in the basket along with the others. The basket was put in an oven at $515C^{\circ}$ to be solution heat treated. After 30 minutes at $515C^{\circ}$, the basket was removed from the oven and put directly in the appropriate cooling fluid. The thermocouples logged the temperature every second during the cooling. The logging continued until the temperature reached a temperature of $100C^{\circ}$ or lower. The solution heat treatment was repeated with new sets of specimens, one for each of the four cooling methods shown in Table 3.2.

Cooling medium	reference
Cold water	Ι
Boiling water	II
Air with fan	III
Still air	IV

Table 3.2: The four cooling mediums used and their reference

After cooling from SHT, all test specimens were naturally aged between 24 and 28 hours before receiving AA heat treatment. The 6063 alloy was aged to peak

hardness. In order to achieve comparable strengths, the alloys had different aging times and temperatures, as shown in Table 3.3.

alloy	SHT time [hours]	SHT temperature $[C^{\underline{O}}]$	AA time [hours]	AA temperature $[C^{Q}]$
6063	0.5	515	7	185
6005	0.5	515	6	205
6106	0.5	515	5	210

Table 3.3: Times and temperatures for solution heat treatment and artificial aging.

3.3 Mechanical Testing

3.3.1 Tensile Testing

Three tensile test specimens were prepared for each of the four heating conditions for the three alloys, a total of 36 tensile specimens. They were all tested in a Zwick Z100 tensile test machine, and the obtained data were plotted as engineering stress vs. engineering strain. The stress-strain curves were further used to determine yield strength, Ultimate tensile strength (UTS) and fracture strain (ϵ_f . The geometry of the tensile specimen is illustrated in Figure 3.1, and the corresponding dimensions are given in Table 3.4. The extrusion direction is in the length direction of the specimen.



Figure 3.1: Tensile specimen geometry with dimensions which are found in Table 3.4 [42].

Table 3.4: Dimensions of the lengths corresponding with symbols in Figure 3.1.

Dimension of specimen	Symbol	dimension length [mm]
Thickness	Т	4
Overall length	L	150
Gauge length	G	40
Reduced parallell section length	А	70
Length of grip section	В	35
Width	W	12.5
Width of grip section	С	18

3.3.2 VDA 238-100 bending test

Three bending tests were performed for every combination of alloy and method of cooling from solid solution heat treatment. A Zwick Z250 machine was used to conduct the testing. The square-shaped specimen with dimensions 50mm x 50mm x 4mm was aligned according to figure Figure 3.2. The piston bending the specimen had a tip with a radius of 0.4mm. The specimen was aligned so that the extrusion direction was parallel to the length direction of the piston tip and thus the bending axis. The force required for the piston to further bend the specimen increases until it reaches a peak. The test stops when the bending force has dropped 60 N from max. Bending force and the downwards movement of the piston are logged, so peak and final bending angle, α can be acquired.



Figure 3.2: Bending test (a) where 1 is the piston, 2 is the specimen, 3 is the bending axis and 4 is the extrusion direction, and a specimen (b) with bending angle α .

3.3.3 Fracture surface area

The fracture surfaces of all tensile specimens of conditions I and II of alloy 6063 were imaged with a ZEISS Stemi 508 stereo microscope. The reduction in surface area at fracture is a measure of ductility. After the tensile tests had been conducted, the surface areas of the fractured tensile specimens were measured and compared to the initial area. Both parts of the fractured specimen of all three tensile specimens for each condition were used. An exact millimeter was imaged to calibrate the microscope and have a precise scale in the images of the fracture areas. This was done when the microscope was in focus to have a precise scale for the applied working distance and magnification. All tensile specimens showed a shear fracture, demonstrating a certain angle between the direction of the tensile force and the normal of

the fracture surface. As the tensile specimens showed shear fractures, a projection of the surface area was imaged.

The microscope was set to be focused in the middle of the fracture as there was some height difference. The software Image J was used to measure the projection of the fracture surface areas. The software was calibrated by measuring the number of pixels in the image's scale bar of 1 mm. The fracture area was marked manually by setting the edges. Then the area function in Image J gave the surrounding area. An example of a marked area is shown in Figure 3.3.



Figure 3.3: Fracture surface area measurement in Image J.

3.4 Optical light microscopy

Bending test specimens from alloy 6063 conditions I and II were inspected in an optical light microscope. The specimen was cut perpendicular to the bending axis with a thickness of ~ 3 cm using a Struers Discotom-5. The samples were ground successively with SiC grinding paper with increasing fineness: 240p, 480p, 800p and 2000p. The specimens were rinsed with water between each step. Polishing was performed with a 3μ m diamond spray and then a 1μ m diamond spray on separate polishing disks. The specimens were rinsed with water and soap after each polishing step. The specimens were then anodized by using an anodizing solution with 5% HBF_4 , an applied voltage of 20V and duration of 90s. After anodizing, the specimens were immediately rinsed with water and then ethanol.

The bending test specimens could then be inspected with a Leica MEF4M optical

light microscope. A λ -plate was inserted and set to the angle, giving the maximum contrast between grains in the image.

3.5 Preparation of TEM-samples

The TEM specimens were made of material from tensile test specimens. Slices with a thickness of 1.1mm were cut from the ends of the tensile specimens perpendicular to the length direction. This material is assumed not to contain any plastic deformation from the tensile test, as it is from a region with a much larger cross-section than the thin middle part. The cutting was done using a Struers secotom-60 saw with a recirculating, corrosion-resistant cooling fluid. The outermost slices cut out from the tensile specimens were discarded. The cut slices were then put in a petri dish with acetone for 15 minutes before being transferred to a new petri dish containing 96% alcohol for another 15 minutes before drying.

The cleaned specimens were then ground and polished with Struers SiC paper using a Struers RotoPol one at a time. Fastening of the specimen to a sample holder was done by using double-sided tape. The grinding paper with the coarsest particles ground off an amount of the thickness of the specimen given in Table 3.5. Controlling the amount of ground material was done by measuring the thickness with a micrometer. The polishing performed in the last two steps also included pushing down a piece of solid soap on the rotating disc in front of the specimen to obtain a smooth and mirror-like surface. After polishing one side, the tape was removed, and the specimen was put in acetone and then ethanol. Then the polished side was glued onto a specimen holder using a thin layer of superglue which was then put into an apparatus that allowed for control of how many μ m were ground away. The same procedure as on the first side was then repeated. To obtain disks with the correct dimensions for the TEM sample holder, discs with a diameter of 3mm were punched out from the specimen using a punching apparatus.

Grinding paper	Thickness ground [mm]	lubricant
p1200	300	water
p2400	100	water
p2400	50	water $+$ Soap
p4000	50	water $+$ Soap

Table 3.5: Grinding and polishing steps for preparation of TEM-samples

An appropriate thickness for specimens to be inspected in TEM is about 100nm [34]. That would be extremely difficult to achieve by mechanically grinding. Therefore electropolishing is used. This method etches off material in the centre of the specimen discs mentioned above. Etching is done by applying a voltage and introducing jets of electrolyte in the center of each side of the disc, which dissolves metal. This results in a crater-like shape with small holes in the centre of the disc on both sides. Etching continues until the amount of light passing through small holes reaches the preset limit. In proximity to these small holes the specimen can be very thin, in the range of of 1-100nm.

In this experiment, a Struers-Tenupol electropolishing unit was used with an electrolyte consisting of $1/3 \ HNO_{3(l)}$ and $2/3 \ CH_{4(l)}$ in parts volume. Before starting the electropolishing, the electrolyte was cooled to -30° with liquid nitrogen. A thermometer was used to control the temperature and kept in the interval, $-25^{\circ}C^{\circ}$ ± $5^{\circ}C^{\circ}$, during the whole etching process. The specimen disc was mounted in a plastic sample holder which was put in the electropolishing unit. The voltage was set to 20V, the light sensitivity to 100 and the flow rate to 20.

After the electropolishing, the plastic container with the specimen was dipped in a 250 ml beaker with methanol. Then the disc was transferred to a new container with 250 ml methanol, where the holder was opened and the disc dismounted. Finally, the disc was put into two petri dishes containing 50 ml of ethanol before drying and being ready for inspection in the TEM. In some discs, the etched hole was large, or the disc was not intact and therefore discarded. Only discs that from visual inspection in a light microscope seemed to have a thin area, had small holes, and no irregular shape was brought to the TEM.

3.6 TEM

3.6.1 CBED- Thickness Determination

The distance between fringes in a CBED pattern can be used to precisely determine the foil thickness of a small area of a specimen. From the dynamical theory of diffraction contrast, there is a relationship between the amplitude of the diffracted wave and the thickness of a thin specimen. The amplitude of the diffracted wave, ϕ_g , is calculated from Equation 14 where $S_{eff} = \sqrt{s^2 + \frac{1}{\zeta^2}}$, is the deviation vector and ξ is the extinction distance of the material [43].

$$\phi_g^2 = (\frac{\pi}{\xi_g})^2 \frac{\sin^2(\pi t s_{eff})}{\pi t s_{eff}}$$
(14)

From an image in two beam condition of a (220) kikuchi-band as Figure 3.4, K-M fringe intensity minimas are obtained where $\phi_g=0$. The deviation vector for fringe number i, s_i , follow the relationship in Equation 15 [43]. Here the wavelength is of the electrons, d_{hkl} is the distance between planes, θ_B is the Bragg angle for hkl plane so $2\theta_B$ is the band width of the Kikuchi-band and $\Delta \theta_i$ is the distance between s=0 and fringe i [34].

$$s_i = \frac{\lambda}{d_{hkl}^2} \frac{\Delta \Theta_i}{2\Theta_B} \tag{15}$$



Figure 3.4: 220 kikuchi band with measurements of band width, Θ_B , and K-M fringes, Θ_i .

By combining Equation 14 and Equation 15 and setting $\phi_g=0$ Equation 16 is found. From plotting $\frac{s_i^2}{n_i^2}$ VS. $\frac{1}{n_i^2}$ which is in the form Y=Ax + b, where b correspond to $\frac{1}{t^2}$ and $\frac{1}{\xi^2}$. The thickness t can thus be can be determined from the point of interception as shown in Figure 3.5.

$$\frac{s_i^2}{n_i^2} = -\frac{1}{\xi_g^2} \frac{1}{n_i^2} + \frac{1}{t^2}$$
(16)

For each thickness measurement in this thesis, three or four θ_i were used to obtain a linear trend line that could be utilized to determine the thickness. R represents how well the line fits the data points. If R=1 the plot is a perfect fit and R decreases with error relted to the sum of the squared error in each point. There are two plots in Figure 3.5 and the right one was chosen to give the right thickness as it had the least error.



Figure 3.5: A plot of $\frac{s_i^2}{n_i^2}$ VS. $\frac{1}{n_i^2}$ with a regression line intercepting the y axis at $\frac{1}{t^2}$

3.6.2 Precipitate statistics

The number density was found by counting precipitates in [001] direction of the aluminium matrix appearing as white dots in DF and determining the volume. Since the precipitates in the Al-Mg-Si system grows along with the three [001] directions, it is assumed that a total of 3 times as many precipitates are present as what can be counted in the [001] direction [18]. Therefore the number of precipitates in Equation 17 equals 3N. ρ is the number density, t is the thickness determined with CBED and the area A, measured directly from the image.

$$\rho = \frac{3N}{At} \tag{17}$$

The studied areas of the specimens were all extremely thin and had thicknesses in the range of 80-180nm. A significant amount of precipitates will therefore be cut off by the specimen surface as illustrated in Figure 3.6. The overestimation of precipitates by cutting is compensated for by adding an imaginary layer on either side of the specimen, $\lambda /2$, when calculating precipitate density giving Equation 18. λ is determined from Equation 19 where l_m is the average precipitate length, ϕ is the angle between the normal of the surface and [001]- zone axis, and θ is the angle between the specimen surface and precipitates which are perpendicular to [001]. Though difficult to measure, $\theta = 45^{\circ}$ has proved to be a good approximation [44].

$$\rho = \frac{3N}{A(t+\lambda)} \tag{18}$$

$$\lambda = \frac{l_m}{1 - (l_m/t)tan(\phi)cos(\Theta)}$$
(19)

Precipitate statistics have been performed for condition I and II of the 6063 alloy. 250 lengths were measured from BF images at 150k magnification for each condition to find the average length. Only precipitates from a predefined area in the images' centres were measured. This was to ensure that measured, long precipitates would not be cut by the image edge and could be measured to their full length. Precipitate density was found by manually counting all precipitates in a Df image with 100k magnification and measuring the thickness in the centre of the image. Five sets of measurements for number density was performed for condition I and II of 6063. Constructing a grid was necessary as the images contained 800-1300 white precipitates in [001]. 150 Cross-sections of both conditions were studied using HRTEM at a magnification of 800k. The area was found by multiplying the lengths of sides of the rectangular precipitates.



Figure 3.6: Illustration of some precipitates being cut by the specimen surface and $\lambda/2$ added on either side of the specimen.

3.6.3 Width of PFZ's

When measuring the width of a PFZ, having the incident beam as close to parallel with the grain boundary projection as possible gives the most precise measurements. As this often proved difficult to achieve by tilting, a large number of grain boundaries were observed and only proceeding with those where the projection of the grain boundary and the incident beam was close to parallel, and then using tilt to minimize deviation. The width measurements were performed by drawing lines of 50nm along with the imaged GB. The next line start where the previous ended. The minimal distance to a precipitate from the 50 nm line on the grain boundary was measured. This was repeated throughout the imaged GB length to find the average PFZ width. Only one side of each grain boundary was measured as both sides appeared to be equal. Measurements were taken from five grain boundaries of condition I, II and IV in the 6063 alloy.

3.6.4 EDS

Particles on grain boundaries and dispersoids were inspected with EDS. The beam used was convergent and covered the particle and slightly more of the surroundings to have the particle as a significant fraction of the inspected volume while still having control of what was illuminated by the beam.

4 Results

4.1 Cooling curves

The only difference in the mechanical treatment given is the cooling rate from SHT. The logged temperature is plotted vs. the logarithm of time for each cooling method in Figure 4.1. The result shows well-distributed cooling rates where still air produces the lowest and cold water the highest.



Figure 4.1: Cooling curves for each of the four cooling mediums: cold water(I), boiled water(II), air with fan(III) and still air (IV) nd applies to all three alloys.

4.2 Mechanical tests

4.2.1 Tensile Test

For alloy 6063, the stress-strain curves from tensile testing is presented in Figure 4.2 and the resulting values for Rp02, UTS and e_f are tabulated in Table 4.1. The yield strength RP02 drops with decreasing cooling rate. The fracture strain is significantly larger for the fastest cooled condition and then drops significantly for the condition cooled in boiled water, where it decreases with decreasing cooling rate.



Figure 4.2: Stress-strain curves from alloy 6063 for each of the four cooling mediums: cold water(I), boiled water(II), air with fan(III) and still air (IV).

Table 4.1: Rp02, UTS and e_f for alloy 6063 and all four conditions

	6063 I	6063 II	6063 III	6063 IV
Rp02 average [MPa]	247 ± 0.94	248 ± 0.82	235 ± 0.47	222 ± 1.2
UTS [Mpa]	263 ± 0	268 ± 0.82	257 ± 0.47	249 ± 0.82
ef []	13.3 ± 0.047	11.6 ± 0.34	11.1 ± 0.34	11.1 ± 0.081

Tensile test results for each condition of alloy 6005 are plotted in Figure 4.3 and main mechanical properties are shown in Table 4.2 In this alloy the fracture strain is largest for condition IV, which has the slowest cooling rate. The yield strength is almost the same for the two quenching conditions in water before it decreases with decreasing cooling rate.



Figure 4.3: Stress-strain curves for each of the four cooling methods from alloy 6005: cold water(I), boiled water(II), air with fan(III) and still air (IV)

Table 4	4.2
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	6005 I	6005 II	6005 III	6005 IV
Rp02 average [MPa]	258 ± 0.82	259 ± 1.2	244 ± 0.82	218 ± 2.5
UTS [Mpa]	272 ± 0.82	276 ± 0.82	267 ± 0.94	248 ± 1.2
ef []	9.43 ± 0.047	9.97 ± 0.17	9.17 ± 0.12	10.33 ± 0.42

Results from tensile testing of alloy 6106 are shown in Figure 4.2, and the extracted mechanical properties are shown in Table 4.2 In this alloy, the fracture strain shows similar behavior to 6063, where condition I with the fastest cooling rate yields the largest fracture strain. Condition II shows a somewhat larger yield strength than condition I. The yield strength drops with a further decrease in cooling rate in conditions III and increasing to IV.



Figure 4.4: Stress-strain curves from alloy 6106 for each of the four cooling methods: cold water(I), boiled water(II), air with fan(III) and still air (IV)

	6106 I	6106 II	6106 III	6106 IV
RP02 [MPa]	263 ± 1.2	269 ± 0.82	248 ± 2.4	220 ± 2.1
UTS [Mpa]	280 ± 0.94	286 ± 1.2	271 ± 1.9	251 ± 1.6

 8.90 ± 0.082

 10.7 ± 0.40

ef [

Table 4.3

 8.30 ± 0.29

 9.47 ± 0.33

4.2.2 Fracture surface area

Images taken with a stereo microscope of fracture surfaces from tensile test specimens in condition I and II are shown in Figure 4.5. Condition I seems more constricted than condition II, which is supported by a larger reduction cross-section area from Table 4.4.



Figure 4.5: Images of tensile specimens fracture surfaces from 6063 I (a) 6063 II, taken with a stereo microscope.

Table 4.4: Reduction of cross section area, q, as compared to initial cross-section of the tensile specimens.

	6063 I	6063 II
q average [%]	36.2 ± 0.69	22.3 ± 1.1

4.2.3 Bending Test VDA238-100

The bending angle α and the maximum force F from the bending test for alloy 6063, 6005 and 6106 are tabulated in Table 4.5, Table 4.6 and Table 4.7 respectively. The alloys showed a significantly larger α for condition I compared to II. All alloys show a decrease in bending angle when the cooling rate starts to decrease from condition I to II, before the bending angle increases with further reduction in cooling rate. Maximum bending angle was achieved in condition I for 6063 and 6106 while in condition IV for 6005.

Table 4.5: VDA 238-100 bending test for alloy 6063 for each of the four cooling condition I-IV, showing values for bending angle (α) and maximum force (Fmax).

	6063 I	6063 II	6063 III	6063 IV
α average [°]	87 ± 0.71	35 ± 0.58	30 ± 0.58	42 ± 1.5
Fmax average [kN]	10.5 ± 0.031	8.34 ± 0.070	7.82 ± 0.013	7.87 ± 0.073

Table 4.6: VDA 238-100 bending test for alloy 6005 for each of the four cooling condition I-IV, showing values for bending angle (α) and maximum force (Fmax).

	6005 I	6005 II	6005 III	6005 IV
α average [°]	47 ± 4.5	28 ± 0.94	28 ± 0.47	52 ± 1.2
Fmax average [kN]	8.54 ± 0.038	8.04 ± 0.036	7.77 ± 0.015	$7.89 {\pm} 0.014$

Table 4.7: VDA 238-100 bending test for alloy 6106 for each of the four cooling condition I-IV, showing values for bending angle (α) and maximum force (Fmax).

	6106 I	6106 II	6106 III	6106 IV
α average [°]	54 ± 1.24	21 ± 0.47	20 ± 0.47	28 ± 0.94
Fmax average [kN]	$9.48 {\pm} 0.11$	8.07 ± 0.029	7.57 ± 0.021	7.29 ± 0.020

4.2.4 Optical Microscopy of Bending Specimens

OM was performed on bending specimens of condition I and II, which showed the largest difference in bending angle. The grains of the stretched side of the specimens in Figure 4.6 are more oblong in condition I than in II. The centres of the specimens show no clear difference between the two conditions in Figure 4.7. In Figure 4.8, images of the compression side, condition I with the largest bending angle, show more deformed grains than condition II.



Figure 4.6: OM of the bending specimens stretched side of 6063 I and 6063 II (b)



Figure 4.7: OM of the bending specimens centres of 6063 I and 6063 II (b)



Figure 4.8: OM of the bending specimens compression side of 6063 I and 6063 II (b)

4.3 TEM results

4.3.1 Precipitate Statistics

The precipitates and their statistics were investigated for conditions I and II of the 6063 alloy. The length of the precipitates was measured from 150k magnification BF images in 001 zone axis as shown in Figure 4.9 (a) and (b). Images with 800k magnification were used to estimate precipitate cross-section area as in Figure 4.9 (c) and (d)



Figure 4.9: Precipitates taken in BF and 001 zone axis of: 6063 I at 150k(a), 6063 II at 150k(b), 6063 I at 800k(c) and 6063 II at 800k(d)

DF images in 001 zone-axis at 100k magnification and CBED images of the 220kikuchi band were taken to estimate the precipitate density of conditions I and II of 6063. Out of the five sets of DF and CBED images for each condition, both had a DF image with a thickness determined to be 94nm shown in Figure 4.10.



Figure 4.10: Precipitates taken in DF and 001 zone-axis of: 6063 I at 100k(a), 6063 II at 100k (b), CBED of 220 kikuchi band of 6063 I (c) and CEBD of 220 kikuchi band of 6063 II (d)

The plots of $\frac{s_i^2}{n_i^2}$ VS. $\frac{1}{n_i^2}$ used to find the thickness from the CBED-patterns in Figure 4.10 are shown in Figure 4.11.



Figure 4.11: Two thickness determinations resulting in the same thickness, 94nm, where (a) is from 6063 I and (b) from 6063 II.

The results from measuring lengths, estimating cross-sections and precipitate densities for condition I and II are shown in Table 4.8. The corrected density is based on Equation 18 and Equation 19. The lengths seem to be the same, while the crosssection of condition I appear to be larger than in II. The density is significantly higher in condition II than I.

Table 4.8: Precipitate statistics of alloy 6063 condition I and II showing the average values and standard deviation of length and cross-section. Measured precipitate density, corrected density and volume fraction of precipitates in the material are shown.

	6063 I	6063 II
length [nm]	34.39 ± 18.5	34.26 ± 22.2
Cross-section $[nm^2]$	8.50 ± 4.63	7.25 ± 4.51
Precipitate density $[n/\mu m^3]$	23773	36332
Corrected density $[n/\mu m^3]$	18578	27530
Volume fraction [%]	0.543	0.687

4.3.2 PFZ

The width of the PFZ around grain boundaries was measured for condition I, II and IV of alloy 6063. Measurements were taken from five different grain boundaries for each condition, and one of them is shown in Figure 4.12. The results are given in Table 4.9. It is clear that the slowest cooling, condition IV, gave the widest PFZ. The average width of PFZ in condition II is significantly larger than in I, but the width is not the exact same along a grain boundary. Some variation between grain boundaries within the same condition was also found and is reflected in the standard deviation.





Figure 4.12: PFZ around grain boundary of alloy 6063 in condition I, II and IV

Table 4.9: PFZ width and standard deviation of alloy 6063, condition I, II and IV $\,$

	6063 I	6063 II	6063 IV
PFZ width [nm]	59.78 ± 6.19	75.3 ± 11.8	142.14 ± 8.13

4.3.3 EDS

Two dispersoids from alloy 6063 in condition II were analyzed with EDS. They are imaged in Figure 4.13 and were analyzed using a convergent beam. The resulting composition are shown in Table 4.10. They both contained significant amounts of Fe, Si and Mn in addition to Al and O. They are likely AlMnFeSi dispersoids.



(a)

(b)

Figure 4.13: Two dispersoids a (a) and b (b) from alloy 6063 in condition II analyzed with EDS $\,$

Element	Dispersoid a [wt $\%$]	Dispersoid b [wt %]
Al	92.05 ± 0.10	87.15 ± 0.10
Ο	2.29 ± 0.06	2.39 ± 0.07
Fe	2.26 ± 0.04	3.13 ± 0.04
Si	1.58 ± 0.04	3.14 ± 0.05
Mn	0.94 ± 0.03	1.19 ± 0.03
Cr	0.06 ± 0.02	0.09 ± 0.02
Cu	0.27 ± 0.02	0.27 ± 0.02
Zn	0.06 ± 0.02	0.09 ± 0.02
Au	0.21 ± 0.05	0.22 ± 0.05
С	0.29 ± 0.04	-
Ni	-	0.09 ± 0.01

EDS was also performed on two particles on a grain boundary from alloy 6063 in condition II. They are imaged in Figure 4.14 and were analyzed using a more convergent beam. The result of the compositions is shown in Table 4.11. Both particles showed significant amounts of Mg and Si in addition to Al, C and O. The particles are likely MgSi precipitates



Figure 4.14: Two particles, a (a) and b(b), on a grain boundary from alloy 6063 in condition II analyzed with EDS

Element	Particle a [wt %]	Particle b [wt %]
Al	74.53 ± 0.16	85.46 ± 0.14
Ο	3.95 ± 0.07	2.63 ± 0.07
Si	2.30 ± 0.04	1.57 ± 0.04
Mg	1.78 ± 0.04	2.08 ± 0.05
Cu	0.25 ± 0.02	0.30 ± 0.02
Zn	0.10 ± 0.02	0.06 ± 0.02
\mathbf{C}	17.04 ± 0.15	7.68 ± 0.11
Ca	0.05 ± 0.01	-
Au	-	0.22 ± 0.01

Table 4.11: Results from EDS of particle a and b from alloy 6063 in condition II

5 Discussion

The different mechanical properties caused by different cooling rates from SHT are the basis for this thesis. The phenomenon will be tried explained through this discussion based on results on a micro-structure level from TEM.

5.1 Mechanical Tests

The fracture strain of alloy 6106, 6063 and 6005 change as a function of cooling rate. Alloy 6106 and 6063 behave similarly, while the 6005 alloy differs in fracture strain with respect to the cooling rate shown in Figure 5.1. 6106 has a higher RP02 strength than 6063 in condition I and II of 16 Mpa and 21 MPa, respectively. The difference in strength can be partly explained by higher contents of copper and magnesium in 6106 [45]. The difference in the strength of the two alloys becomes smaller in condition III. In condition IV 6063 is slightly stronger. 6106 is expected to be somewhat overaged as AA was performed on a 25°C higher temperature. The AA time was shorter for 6106, but sufficient to exceed peak hardness with the applied temperature. Overaging implied a lower tensile strength and was done to achieve a more similar Rpo2 strength for the alloys. The strength is imperative when comparing ductilities as they are directly related. 6106 has a somewhat lower Rp02 strength and is expected to have a lower e_f than 6063.

The difference in Rp02 is slight for all the three alloys, a maximum of 6 Mpa when comparing condition I and II within an alloy. Therefore the strength difference does not need to be taken in special consideration when comparing e_f between condition I and II within an alloy. Alloy 6005 showed an increase in e_f of 0.5%, going from condition I to II. The alloy was aged with a time and a temperature between the ones used for alloy 6063 and 6106. The amount of alloying elements in 6005 was also in between the two other alloys and was low in copper as 6063. 6005 do contain more Mn than the two other alloys which could which could be an explanation. All three alloys have recrystallized grain structures.



Figure 5.1: e_f as a function of condition (decreasing cooling rate from SHT) from alloy 6063, 6106 and 6005.

The three studied alloys all show a similar evolution of bending properties when decreasing the cooling rate from SHT Figure 5.2. Alloy 6063 exhibits the most significant reduction in bending angle when going from condition I to II. It is also the alloy with the least alloying elements. The least pronounced change of α from condition I to II is in alloy 6005. This was also the case for e_f from the tensile test. This means 6005 is the alloy that shows the least favorable change in the two ductility parameters in this study by having a very rapid cooling rate from SHT. Based on tensile and bending testing, 6063 produce the most significant increase in the ductility parameters.

The better ductility of 6063 conditions I compared to II was further substantiated by a reduction in cross-section area at fracture. A 14% larger reduction in area in condition I than II correlates as expected with a significantly larger fracture strain [46]. Further evidence of an increased ductility in condition I is given from OM of the bending specimens. The OM images revealed more elongated grains on the stretched side of the bending specimen and smaller deformed grains on the compressed side in condition I.



Figure 5.2: Bending angle α from the bending test as a function of condition (decreasing cooling rate from SHT) of the investigated alloys.

5.2 TEM

Limited time to obtain data for precipitate statistics restricted the choice to investigate one alloy for TEM-characterization. The choice fell on 6063 as this alloy shows the most significant improvement in ductility in both the VDA238-100 bending test and in fracture strain from the tensile test.

5.2.1 Precipitates Characteristics and Statistics

Increased cooling rate from SHT would lead to more solute and vacancies in SSSS, which are prerequisites for nucleation. Therefore one would expect a fast quenching rate to increase the precipitate number density. The results from precipitate statistics with five measurements from each of the two conditions of alloy 6063 and a total of over 9000 counted precipitates showed the contrary. A fast quenching rate reduces the number density. Consequently, there is reason to believe that some other mechanism affects nucleation. Studies have earlier been performed on the effect of pre-aging of Al-Mg-Si alloys at 70°C. Atom probe tomography revealed increased GP-zones after pre-aging and before AA. Higher number density of β " was found after AA with TEM-analysis [21]. One can speculate on a similar effect caused by a slower cooling rate when comparing conditions I and II of this thesis. If some more diffusion is allowed before reaching room temperature, this can result in the formation of GP-zones and thus more β ".

An increased number of precipitates should be associated with increased precipita-

tion hardening. Significant differences in number densities were observed between conditions I and II of alloy 6063, while Rp02 strength of the two conditions was practically the same. The simplest way of looking at this would be to treat the grains as composites. Where the total strength is decided by summing up the total strength contribution of each area multiplied by its area fraction. PFZs are softer than grain centers with precipitates. This consideration is probably oversimplified. The condition with the highest precipitate density and precipitate volume fraction also had more PFZs. The different amounts of PFZ have an equalizing effect on the total number of precipitates in the two conditions. The total area of PFZ in the grains in conditions I and II appeared to be small, so the effect of PFZs reducing the total number of precipitates is not expected to be prominent. A Lower volume fraction of precipitates should also imply more atoms in solid solution which also have a strengthening effect while smaller than the effect from precipitation.

Most precipitates studied in HRTEM at 800k in condition I and II of alloy 6063 could be recognized as β " due to its characteristic angle of 105° and monoclinic structure [47]. Examples of the precipitates are given along with an image from literature for comparison in Figure 5.3. Observing mostly β " is expected as the 6063 alloy is aged to peak hardness. It should also be noted that in condition IV, larger precipitates was seen than what was observed in in I and II Figure 5.4



Figure 5.3: β " precipitates from 6063 I (a), 6063 II (b) and from literature [47] (c)

5.2.2 DF counting

Some parameters may effect the number of counted precipitates. The degree of darkness in the background of the DF images used for counting white 001-precipitates varied among the analyzed images. The black and white contrast in the DF image is advantageous to distinguish small precipitates from matrix. Larger average crosssection of precipitates might lead to a slightly better detection rate in condition I than II. The thickness was measured in the centre of each DF image and local variation in thickness compact the resulting number density. Presence of favoured nucleation sites could effect the the

5.2.3 Thickness Measurement

The measurements of the width of KM-fringes did not always give a perfect fit. Sometimes the best possible fit and the second-best were quite close in terms of R-value. In these cases, a simulation based on dynamical theory was used to decide which plot was correct. The simulation of the fringes around the 220 Kikuchiband starts at 30 nm specimen thickness and goes up to 180nm. A thickness was acquired by comparing the simulation at a thickness where the simulated diffraction pattern was equal to the imaged CBED pattern by visual inspection. This thickness was close to the thickness in one of the two best fits for all cases except for one case, where the thickness was undeterminable. This was for measurement 4 of condition II Figure B.2. The extinction distance should be constant and not change with specimen thickness. The extinction distance changes in the CBED pattern in this thesis and is an additional source of error. However, it has been found that the resulting thickness is not sensitive to the extinction distance by the TEM Gemini group at NTNU where several researchers use the CBED technique to acquire thicknesses of aluminium specimens.

5.2.4 PFZ Width

The width of the measured PFZ in alloy 6063 increased from condition I to condition II and drastically to condition IV. PFZs are expected to increase in width with increased cooling rate from SHT. A large cooling rate enables to "freeze in" more vacancies and solute compared to a slower rate. A Grain boundary functions as a sink draining out solute and vacancies by diffusion. When diffusion is increased, more solute and vacancies will be drained to the grain boundary. The concentration of vacancies and solute decreases in the proximity of the grain boundary. The critical concentration needed for nucleation of precipitates is then moved further away from the grain boundary and thus increasing the width of the PFZ. The quantitative difference in PFZ width between condition I and II is not that clear as the standard deviations are quite high, but the results indicate some difference. Grains have varying orientation relations, and the grain boundary plane can have many directions. Therefore grain boundaries will have different characteristics. Some have precipitates with varying sizes and distances, and some boundaries have no precipitates at all. When moving along a grain boundary, its plane will change and different characteristics may be observed.

Differences in PFZ width and ductility properties as bending angle and fracture strain have been found. Previous studies have found that a narrower PFZ could

increase or decrease ductility depending on the fracture mode. If intergranular fracture is significant, a wide PFZ around the grain boundary can promote ductility as a larger soft zone can relieve more stress in front of slip bands near a grain boundary. A narrow PFZ reduces the risk of strain localisation around the grain boundary. [33]. The results of this thesis correspond to a narrower PFZ in condition I increasing the ductility. However, other mechanisms might also be affecting the ductility and thus making the effect more complicated to deduce. Characterizing the fracture mode would be advantageous to better evaluate the effect of PFZ width for this material. The material would be expected not to show significant intergranular fracture if the proposed theory holds.

The condition cooled in still air from alloy 6063 showed a different structure within grains compared to conditions I and II. This is depicted in Figure 5.4 where one can see precipitates nucleating on dislocations with PFZs around them. Some dislocations are always present and represent favorable sites to nucleate for precipitates. The dislocations can be spotted by observing lines of small precipitates. Solute and vacancies are most likely drained to where nucleation occurs, leaving a PFZ around the dislocation. PFZs around dislocations were observed frequently in condition IV, only once in condition II and never in condition I. Therefore, the phenomenon is likely related to the cooling rate from SHT and could be related to the increased diffusion before the material reaches room temperature when cooling slowly.



Figure 5.4: PFZs around dislocations and precipitates of alloy 6063 in condition IV at 50k magnification

5.2.5 PFZ Measurements

As mentioned before, the grain boundary plane is changing when moving along it and are formed between grains with different orientation relations. To have perfect conditions to measure the PFZ around a grain boundary, the plane of the grain boundary should be parallel with the incident beam. In this case, the grain boundary is seen as a thin line. If the grain boundary plane and the incident beam are not perfectly aligned, the grain boundary appears thicker and the PFZ narrower. Increasing misorientation between the incident beam and grain boundary plane results in a decreased measured PFZ and higher error. The measured PFZ divided by the actual width will be proportional to the cosine of the misorientation between the incident beam and grain boundary plane.

The thickness of the specimen in the area of the PFZ will also have some influence on the measured width of PFZ. When considering a thin specimen, the distance from a certain point on the grain boundary to the closest precipitate is likely to be larger as there are fewer precipitates in a thin specimen. To obtain perfect alignment of grain boundary plane and the incident beam by tilting the specimen proved to be difficult in most situations. A tactic that proved viable for obtaining the most accurate measurements was observing many grain boundaries and only proceeding with those which showed minor misalignment in the zone axis. i.e. the grain boundary appeared as or close to, a thin line. And then adjusting with some tilting to make alignment slightly better if possible. The grain boundaries appeared as relative thin lines in the images used for acquiring results. The measurements should therefore have good validity.

5.2.6 Particles on grain boundary

The particles depicted in Figure 4.14 which were analyzed were particles on a grain boundary. The EDS-analysis in Table 4.11 suggests they do not contain Fe or Mn, but are high in Mg and Si. This indicates that particles are not dispersoids but rather a phase in the sequence given in Equation 4. Occasionally, grain boundaries had particles evenly distributed along the grain boundary. Grain boundaries were often observed without precipitates at all and other times with larger particles with less even distribution than in the case of small particles. As the orientation differences between two neighboring grains can differ quite a lot, so will the strain misfit energy and the potential for a particle to nucleate on the grain boundary. Comparable studies on quenching rate from SHT of a 6016 alloy have found coarser Mg_2Si and Si particles on grain boundaries for slower cooling than fast [48]. Parallel behavior was found regarding a reduction in bendability associated with a decrease in cooling rate. Coarser Mg_2Si and Si particles are favoured by slower cooling and making crack propagation more rapid [49]. As no clear trend of particles on grain boundaries was observed from visual inspection in this thesis, a quantitative analysis of grain boundary particles should be performed in order to see if there is a similar mechanism in the 6XXX alloys studies in this thesis.

The dispersoids in Figure 4.13 where investigated with EDS to confirm which elements they contained. They contain significant amounts of Fe and Mn which are expected to mostly be in these particles rather than the matrix.

5.3 Further Work

Based on the results and discussion of this thesis, some experiments could provide information to find answers to what causes the change in ductility going from a rapid cooling rate to a bit slower. These are listed below:

- Investigating alloy precipitate statistics as well as PFZs in 6005 and 6106 in TEM.
- Quantative studies of particles on grain boundaries
- Fracture mode characterization
- Investigating the effect of Mn additions and dispersoid as the alloy which shows least changes ductility has the highest amount of Mn.

6 Conclusion

Experiments were performed to understand better the effect of cooling rate from SHT on the ductility of Al-Mg-Si alloys. Mechanical testing was conducted for three alloys, 6063, 6005 and 6106, where only the 6063 was further analyzed with OM, stereo microscope and TEM. Precipitates, grain boundaries and PFZs were analyzed with TEM. The following conclusions can be drawn on the basis of the obtained results:

- The three studied alloys all showed significantly better bendability in the condition quenched in cold water than in the condition cooled in boiled water. All alloys had comparable strength in those two conditions.
- The 6063 alloy showed the highest response in ductility increase in terms of fracture strain and bending angle. The fastest cooled condition showed a significant higher area reduction of cross-sections of tensile test specimens at fracture and OM of the bending test specimen revealed more deformed grains.
- Significantly lower precipitate density was found in the fastest cooled condition compared to the second fastest cooling.
- The precipitate lengths were found to be unaffected by the cooling rate from SHT, while there were indications of larger cross sections in the fastest cooled condition.
- The width of PFZ around grain boundaries was found to increase with a decreasing cooling rate. The mechanical results propose that a narrow PFZ is advantageous in this material, while analysis of the fracture mode should be done before concluding.
- Spherical particles containing Mg and Si were found on grain boundaries. Revised literature proposes that the coarsening of these particles and Si particles on grain boundaries affect the material's bendability. Quantiatve analysis must be performed to investigate how this alloy is effected.

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A Appendix

This appendix show results from density measurements.

Id	t[nm]	n	Area [nm ²]	density[n/ μm^3]	tilt	corrected density
1	150.2	910.5	695055.69	24023.59493	15.88056313	19373.23089
2	94.5	918.5	695055.69	25189.25715	7.591701276	18294.47851
3	139.3	1214.5	695055.69	25268.21134	10.96700834	20125.2653
4	103.3	1304	695055.69	20975.14865	12.79999043	15516.90498
5	189.3	820.5	695055.69	23211.26531	1.910409374	19629.49433

A.1 Density Measurements 6063 I

A.2 Density Measurements 6063 II

Id	t[nm]	n	Area [nm ²]	density $[n / \mu m^3]$	tilt	corrected density
1	94.2	910.5	694472.4095	417537.326	11.74211428	30164.97991
2	114	918.5	695055.69	347757.0644	11.89960218	26454.03947
3	153.9	1214.5	695055.69	340612.4758	17.17129134	27603.1867
4		1304	695055.69		11.60928781	
5	101.9	820.5	695055.69	347541.0054	4.031078531	25899.28373

B Thickness plots

B.1 6063 I



Figure B.1: Plots for obtaining thickness of 6063 I for measurement Id 1 (a), Id 2 (b) ,Id 3 (c), Id 4 (d), Id 5 (e)





Figure B.2: Plots for obtaining thickness of 6063 II for measurement Id 1 (a), Id 2 (b) ,Id 3 (c), Id 4 (d), Id 5 (e)