Grain boundary phenomena and failure of aluminium alloys
Haas, Marc-Jan de

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Chapter 3

GRAIN BOUNDARY PRECIPITATION
IN AA6061 AND AA7050

3.1 INTRODUCTION

Aluminium alloys became more widely used in the last decade. The largest expansion being in the building/construction field, but also in aerospace and automotive applications significant advances have been achieved. As the ultimate tensile strength of aluminium in purest form is of the order of 50 MPa, alloying elements are added in order to enhance strength and hardness. An ultimate tensile strength of about 300 MPa is typical for medium-strength alloys is, whereas the strength is further enhanced to 500 MPa for the high strength alloys. As already mentioned in Chapter 2, the main alloying elements for the 6XXX- and 7XXX series alloys are Mg, Si, Zn and Cu, mainly for precipitation strengthening. Furthermore, Fe, Cr, Mn and sometimes Ni are added for the formation of intermetallic phases acting as grain refiners and slip dispersers [1,2].

During the past decades, the matrix precipitation sequences have been extensively studied. Less is true, however, for the grain boundary precipitates. Although precipitation at the grain boundaries does not significantly contribute to hardening and strengthening, it may have a large impact on properties such as toughness and ductility (Chapter 5 of this thesis). As the chemical composition of the grain boundary is different from that of the matrix, structure and composition of grain boundary precipitates formed during artificial ageing may be distinct from the matrix precipitates.
It was found [3] that atom-probe field-ion microscopy (APFIM) was an appropriate technique for analysis of very fine precipitates (< 5 nm), while energy-dispersive spectrometry (EDS) could be used satisfactorily for precipitates larger than 30 nm. However, with the advent of the field emission transmission electron microscope, nowadays the electron probe can be reduced to ~ 0.5 nm. The dimensions of the grain boundary precipitates are of the order of tens of nanometers and therefore local probe analytical transmission-electron microscopy (TEM) is one of the most suitable tools in order to study chemical composition, precipitate structure and grain boundary misorientation simultaneously.

In this chapter, the morphology of grain boundary precipitates of the commercial aluminium alloys AA6061 and AA7050 will be investigated and differences with respect to matrix precipitates will be discussed. In order to model the growth and distribution of these phases (Chapter 4 of this thesis), both chemical composition and crystallographic structure need to be understood. It was reported [4,5] that grain boundary energy, mobility and diffusivity depend on the grain boundary structure, which is reflected in its axis, angle and plane of misorientation. Structural effects on grain boundary precipitate properties will therefore be studied as well. A factor that is of significant influence on interfacial energy, and thus on precipitate growth, is the crystallographic orientation relationship between the precipitate and the matrix, which will be investigated in the last part of this chapter. Aforementioned characteristics are assumed [6] to play a significant role in the plastic deformation of the alloy.

### 3.2 Matrix precipitation sequences and orientation relationships

#### 3.2.1 Precipitation in 6XXX-series alloys

Matrix precipitation in 6XXX-series alloys has been studied for more than five decades, because of its primary role on the mechanical properties. Different kinds of rod-shaped precipitates have been observed and their crystal lattices have been determined by transmission electron microscopy. Addition of Cu to the 6XXX series alloys was reported [7] to improve mechanical properties due to finer matrix precipitation of the β'-phase and it was found by Edwards, Perovic and Cayron [8-10] that Cu may also be incorporated in this phase.
The proposed transformation mechanisms for precipitation in Al-Mg-Si alloys with and without additional Cu or Si are listed in Table 3.1. The precipitation sequence for Al-Mg-Si is fairly well known. For Al-Cu-Mg-Si alloys, a model of structural phase transitions was proposed by Cayron [11,12] to explain the common substructure of the Q, QC and QP phases. These phases are also reported to coexist in the same precipitate [11].

### Table 3.1: Precipitation sequences in 6XXX-series alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>[Mg]/[Si]</th>
<th>Structure</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Mg-Si</td>
<td>β&quot;</td>
<td>Monoclinic</td>
<td>α = 15.2 Å, b = 4.05 Å, c = 6.7 Å, β = 105°</td>
</tr>
<tr>
<td></td>
<td>β'</td>
<td>HCP</td>
<td>α = 7.05 Å, c = 4.05 Å</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>Mg₂Si</td>
<td>α = 6.42 Å</td>
</tr>
<tr>
<td>Al-Cu-Mg-Si</td>
<td>QP</td>
<td>HCP</td>
<td>α = 3.93 Å, c = 4.05 Å</td>
</tr>
<tr>
<td></td>
<td>QC</td>
<td>HCP</td>
<td>α = 6.70 Å, c = 4.05 Å</td>
</tr>
<tr>
<td></td>
<td>Q</td>
<td>HCP</td>
<td>α = 10.4 Å, c = 4.05 Å</td>
</tr>
<tr>
<td>Al-Mg-Si (Si in excess)</td>
<td>A</td>
<td>HCP</td>
<td>α = 4.05 Å, c = 6.7 Å</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Orthorhombic</td>
<td>α = 6.8 Å, b = 7.9 Å, c = 4.05 Å</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>HCP</td>
<td>α = 10.4 Å, c = 4.05 Å</td>
</tr>
</tbody>
</table>

An interesting point is the presence of Cu in the Q-phase crystal \((\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5)\). According to Arnberg and Aurivilius [16], the Q-structure is close to the Th₇S₁₂ structure, the positions of the Si atoms being nearly the same as those of the Th atoms, and the positions of the (Al, Mg) atoms being nearly the same as those of the S atoms. The only difference is that the \((2/3, 1/3, 1/2)\) and \((1/3, 2/3, 0)\) positions are occupied by the Cu atoms in the Q-structure and are empty in the Th₇S₁₂ structure. Therefore the existence of a Q-structure without or with less Cu, but possibly empty or occupied by Si atoms, seems to be possible. In fact, such a phase is reported in Al-Mg-Si alloys with Si in excess and designated as C-phase \((\text{(Cu,Si)}_8\text{(Mg,Al)}_{13})\) [15-19]. Its low \([\text{Mg}]/[\text{Si}]\) levels seem to confirm the capability for Si to replace Cu in the subunit triangular QP clusters for type A, B and C phases.
The reported orientation relationships between $\beta'$ precipitates and the Al-matrix are: $[001]_{\beta'} // [001]_{\text{Al}}$ and $(100)_{\beta'} // (110)_{\text{Al}}$ or $[001]_{\beta'} // [001]_{\text{Al}}$ and $(100)_{\beta'} // (100)_{\text{Al}}$ [20-22]. The notation for the planes and directions of the HCP structure is according to: $[hkil] \Rightarrow [hkl]$. This notation will be used from now on for the hexagonal structure in this chapter. The reported orientation-relationship of the Q- or C-phase with the Al matrix is [11]: $[001]_{\text{Q}} // [001]_{\text{Al}}$ and $(210)_{\text{Q}} // (100)_{\text{Al}}$.

### 3.2.2 Precipitation in 7XXX-series alloys

The precipitation sequence in 7XXX-series alloys can generally be described according to Table 3.2 [23]. The most common hardening phase here is MgZn$_2$. This phase is the prototype of the hexagonal Laves phase. Because of the much higher Cu-content of some of the alloys from the 7XXX-series alloys, for instance the AA7050 alloy, part of the Zn in the precipitates may be replaced by Cu and/or Al, so that their actual composition is closer to Mg(Zn,Cu,Al)$_2$ [7]. The crystallographic structure of these precipitates, on the other hand, will not change significantly. A variety of orientation relationships between the $\eta$-phase and the matrix have been reported. Indications are that when $\eta'$ is the precursor of $\eta$, the following orientation relationship for $\eta$ applies [23]: $[001]_{\eta} // [111]_{\text{Al}}$ and $(100)_{\eta} // (110)_{\text{Al}}$.

### Table 3.2: Precipitation sequence in 7XXX-series alloys

<table>
<thead>
<tr>
<th>Guinier Preston zones</th>
<th>Monoclinic</th>
<th>Hexagonal</th>
<th>Hexagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta'$</td>
<td>$a = b = 4.97 \text{ Å}, c = 5.54 \text{ Å}, \gamma = 120^\circ$</td>
<td>$a = 4.96 \text{ Å}, c = 8.68 \text{ Å}$</td>
<td>$a = 5.15-5.22 \text{ Å}, c = 8.49-8.56 \text{ Å}$</td>
</tr>
</tbody>
</table>
3.3 Processing routes and experimental procedures

The chemical composition of the AA6061 alloy is 1.0 at% Mg, 0.7 at% Si, 0.15 at% Cu, 0.2 at% Cr, 0.15 at% Mn and 0.7 at% Fe. The as-received alloy was homogenised for 6 h at 565 °C and rolled to 200 µm (88 % rolling reduction). Discs with a diameter of 3 mm were punched and these were subjected to a solution heat treatment at 560 °C for 25 minutes. Subsequently, a water quench was applied and the discs were artificially aged at 160 °C for times up to 195 h.

The chemical composition of the AA7050 alloy is 2.7 at% Mg, 5.8 at% Zn, 2.3 at% Cu, 0.04 at% Cr, 0.10 at% Mn and 0.15 at% Fe. The as-received alloy was homogenised for 6 h at 480 °C and rolled to 200 µm (88 % rolling reduction). Discs with a diameter of 3 mm were punched and were subjected to a solution heat treatment at 480 °C for 25 minutes. Subsequently, a water quench was applied and the discs were artificially aged at 160 °C for times up to 100 h.

Thin foils for transmission electron microscopy were prepared by using a TENUPOL electropolisher containing an electrolyte of 30 % nitric acid in methanol at -20 °C. The polishing voltage was 20 V. Afterwards, the samples were milled with 4 keV Ar⁺-ions under an incidence angle of 6 ° for a few minutes to remove the bent edges and to clean the sample.

The images and selected-area electron diffraction (SAED) patterns were recorded in a JEOL 2010FEG 200 kV analytical transmission electron microscope. As the minimum diameter of the electron probe in this microscope is ~ 0.5 nm, very localized chemical analysis is possible. However, for the determination of grain boundary precipitate compositions by energy dispersive spectrometry in this work, a 1.0 nm electron probe was used. This was done in order to obtain a sufficiently large yield of characteristic X-rays.
CHAPTER 3

3.4 PRECIPITATION AT RANDOM HIGH-ANGLE GRAIN BOUNDARIES

3.4.1 Crystallographic structure and chemical composition of grain boundary precipitates during artificial ageing

The crystallographic structure of grain boundary precipitates in AA6061 was determined for different artificial ageing times. After 0.5 h at 160 °C, it was measured by high-resolution transmission electron microscopy, because the precipitates were still too small to obtain structural information by selected-area electron diffraction. A hexagonal structure with \(a = 10.4 \text{ Å}\) and \(c = 4.0 \text{ Å}\) was found. This structure corresponds closely to that of both the Q-phase and of the C-phase (Table 3.1). With further ageing, no structural changes were observed.

For AA7050, the grain boundary precipitate structure after ageing for 0.5 h at 160 °C was found to be hexagonal with \(a = 4.8 \text{ Å}\) and \(c = 8.7 \text{ Å}\) (close to \(\eta'\)). After ageing for 5 h, the lattice parameters had changed to \(a = 5.1 \text{ Å}\) and \(c = 8.6 \text{ Å}\) (close to \(\eta\)). No structural changes were observed during further ageing.

The major part of the grain boundary precipitates in AA6061 consists of Mg, Si, Cu and Al. A significantly smaller group is composed of only Mg and Si and according to its structure it must be the \(\beta'\)-phase. Chemical analysis will be focussed on the former group. For AA7050, the observed precipitates all consisted of Mg, Zn, Cu and Al. Accurate quantification of the amount of Al in these precipitates is difficult because spurious effects from the Al-matrix always affect the spectrum. In order to minimize these effects, a relative concentration of a solute element with respect to all solutes present, is calculated. For example, the relative Mg-concentration in precipitates of AA6061 is calculated according to

\[
[Mg]_{rel} = \frac{[Mg]}{[Mg] + [Si] + [Cu]} \tag{3.1}
\]

Table 3.3 and 3.4 list the relative solute concentrations for grain boundary precipitates in AA6061 and AA7050, respectively with ageing time. The number of grain boundary precipitates analysed, the number of different random high-angle grain boundaries and the final standard deviation in the relative concentrations, based on an error of 10 % for one acquisition, are tabulated as well.
Table 3.3: Average relative solute concentrations for grain boundary precipitates in AA6061 after several artificial ageing times at 160 °C

<table>
<thead>
<tr>
<th>Time at 160 °C (h)</th>
<th>([Mg]_{\text{rel}})</th>
<th>([Si]_{\text{rel}})</th>
<th>([Cu]_{\text{rel}})</th>
<th>Precipitates analysed</th>
<th>GBs analysed</th>
<th>Stand. Dev. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.5</td>
<td>0.671</td>
<td>0.286</td>
<td>0.043</td>
<td>79</td>
<td>8</td>
<td>1.4</td>
</tr>
<tr>
<td>100</td>
<td>0.653</td>
<td>0.289</td>
<td>0.058</td>
<td>77</td>
<td>9</td>
<td>1.4</td>
</tr>
<tr>
<td>194.5</td>
<td>0.642</td>
<td>0.287</td>
<td>0.071</td>
<td>64</td>
<td>5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3.4: Average relative solute concentrations for grain boundary precipitates in AA7050 after several artificial ageing times at 160 °C

<table>
<thead>
<tr>
<th>Time at 160 °C (h)</th>
<th>([Mg]_{\text{rel}})</th>
<th>([Zn]_{\text{rel}})</th>
<th>([Cu]_{\text{rel}})</th>
<th>Precipitates analysed</th>
<th>GBs analysed</th>
<th>Stand. Dev. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.5</td>
<td>0.546</td>
<td>0.376</td>
<td>0.078</td>
<td>97</td>
<td>9</td>
<td>1.2</td>
</tr>
<tr>
<td>51</td>
<td>0.545</td>
<td>0.382</td>
<td>0.073</td>
<td>87</td>
<td>8</td>
<td>1.3</td>
</tr>
<tr>
<td>100</td>
<td>0.550</td>
<td>0.380</td>
<td>0.070</td>
<td>108</td>
<td>11</td>
<td>1.1</td>
</tr>
</tbody>
</table>

As Table 3.3 and 3.4 point out, the relative solute concentrations in the grain boundary precipitates are changing with artificial ageing time, whereas the crystallographic structure on the other hand, does not alter. The final standard deviations in the concentration values are small enough to validate the trends observed.

For the AA6061 alloy, the relative Mg-concentration is largest at 23.5 h of ageing (i.e. 0.671). It decreases slightly with ageing time to 0.642, but this value is still larger than the largest possible value of 0.62 on the basis of the reported composition of the C-phase without Al (Table 3.1). A possible explanation for this discrepancy would be that Cu and Si may also be substituted by Mg. In contrast to the crystallographic structure, the composition of the grain boundary precipitates would then be different from that reported for the matrix precipitates. As their peaks are closely spaced in the energy spectrum, another explanation may be fluorescence of Mg by X-rays of Al [24], although the fluorescence yield for light elements is low (~0.01 for Mg). From Table 3.3, the relative Cu-content can be seen to increase with ageing time, whereas the Si-concentration does not change significantly.
Before chemical analysis of the grain boundary precipitates in AA6061, they were oriented such that their length direction was almost parallel to the direction of the electron beam. In this way, the electron beam traverses the precipitate along its length and the largest yield of X-rays characteristic for that precipitate is obtained. The decreasing relative concentration of Mg with ageing time, and thus with precipitate growth, might be an indication that the outer ends of the precipitate (i.e. the parts which were added to the precipitate during the latest stage) contain less Mg than the central parts. The observations may thus be explained by the Mg-supply to the grain boundary decreasing relatively faster than the Si-supply and the Si-supply decreasing relatively faster than the Cu-supply during ageing. This idea is depicted qualitatively in Fig 3.1. From the chemical description of the C-phase (Table 3.1), it can be seen that next to Cu and Si also Mg and Al are interchangeable. In this way, the relative concentration of Si can increase with respect to that of Mg and decrease with respect to that of Cu. The chemical composition of the precipitates then apparently is influenced by the relative supply of the solute elements.

Fig 3.1:
Decays in supply of different solutes in AA6061 with ageing time.

A variation in the chemical composition for the same crystallographic structure was also observed within one particle. Fig 3.2a depicts a large grain boundary phase (~ 2 μm length) in a sample that was air-cooled after the solution heat treatment and subsequently aged for 23 h at 160 °C. Extensive grain boundary precipitate nucleation and growth then already occurs during the slow cooling process. The structure at all parts of the particle was found to be hexagonal with \( a = 10.4 \, \text{Å} \) and \( c = 4.1 \, \text{Å} \). The chemical composition, on the other hand, varies significantly, as can be seen from Fig 3.2b. Here, the relative Mg-, Si- and Cu-concentrations are plotted for different equidistant locations on the particle, which are given in Fig 3.2a. Especially the relative Mg- and Si-concentration can be seen to vary significantly along the grain boundary phase.
When the Al-concentration of the phase increases, the relative Mg-concentration decreases, which would result in an increase of the relative Si- and Cu-concentration according to the corresponding equations analogous to equation (3.1). In this phase however, only the relative Si-concentration seems to have increased by a factor of ~ 2.4 at the edges (spot 1 and 5). The relative Cu-concentration on the other hand, increases with a much smaller factor. This would not be expected if only Mg is substituted with Al and it thus strongly supports the idea that when Mg is replaced by Al, simultaneously Cu is replaced by Si. As the C-phase may well exist without the presence of Cu, this substitution of Cu by Si can well be expected. When it is assumed that the phase grows in both directions along the grain boundary, the smaller relative Mg-content at the edges of the grain boundary phase may be an indication that the supply of Mg decreases during growth, just as was observed for the grain boundary precipitates at different stages of artificial ageing (Table 3.3).

For AA7050, only the relative Cu-concentration decreases with artificial ageing time (Table 3.4), whereas the crystallographic structure does not alter. After 100 h at 160 °C, the Cu-supply from the matrix may have decreased relatively more than that of Mg and Zn, which causes the relative concentration of Cu in the grain boundary precipitates to decrease. It can be understood that the relative Mg-concentration will not change significantly, because its absolute concentration in the precipitate is fixed at 33.3 at%.
In addition, sufficient Zn-supply to the growing precipitate may be guaranteed because of its large matrix concentration (5.8 at%). The matrix concentration of Cu (2.3 at%), on the other hand, is much lower so that its relative concentration in the precipitate may decrease with ageing time. Because the \([\text{Mg}]/[\text{Zn}]\)-ratio of the grain boundary precipitates remains about constant throughout the artificial ageing sequence and as the chemical composition of the grain boundary precipitate most probably is \(\text{Mg}(\text{Zn,Cu,Al})_2\), the loss of Cu during ageing may be compensated for by additional Al.

3.4.2 Absolute concentrations of alloying elements in grain boundary precipitates

For the grain boundary precipitates in AA6061, the average \([\text{Mg}]/(\text{[Si]}+\text{[Cu]})\) ratio during artificial ageing is 1.9 (from Table 3.3). Regarding the chemical configuration of the C-phase (Table 3.1), Al would then not be present at all in the grain boundary precipitates and the composition would be \(\text{Cu}_{1.3}\text{Si}_{6.7}\text{Mg}_{15.2}\). However, as mentioned earlier, fluorescence effects may as well explain the larger Mg-concentration. On the contrary, the relative Mg-concentration is 0.16 at the edges of the grain boundary phase of Fig 3.2, so that the composition at these regions corresponds to \(\text{Cu}_{0.8}\text{Si}_{7.2}\text{Mg}_{15.5}\text{Al}_{11.5}\). A broad range thus exists in which the composition of the C-structure may vary, without a change in crystal structure.

Regarding the crystallographic structure of the grain boundary precipitates and the elements present within them, it can be concluded that the phase present at the grain boundaries of AA7050 is \(\text{Mg}(\text{Zn,Cu,Al})_2\). As mentioned earlier, this phase is derived from the \(\text{MgZn}_2\) phase, which has the same structure. Part of the Zn however, is substituted by Cu and Al. Inspection of the chemical formula reveals that the absolute Mg-concentration of the precipitate is fixed and equal to 33.3 at%. This fact enables a quantification of the absolute concentrations of all elements present within the precipitate. The average experimental relative Mg-, Zn- and Cu-concentrations are about 0.543, 0.383 and 0.074, respectively. From these values, the \([\text{Mg}]/[\text{Zn}]\)- and \([\text{Mg}]/[\text{Cu}]\)-ratios are calculated to be 1.42 and 7.34. The absolute concentrations of Zn and Cu can then be determined to be 23.5 at% and 4.5 at%, respectively. Consequently, the absolute concentration of Al in the precipitate must be equal to 38.6 at% and the grain boundary phase can be described as \(\text{MgZn}_{0.7}\text{Cu}_{0.1}\text{Al}_{1.2}\).
Because the absolute concentration of Mg in the grain boundary precipitates is larger than that of the other solute elements, for both alloys, it may act as the rate-controlling element during precipitate nucleation and growth, depending on its grain boundary concentration profile and diffusivity. This point will be further discussed in Chapter 4.

3.4.3 Spread in precipitate composition

Because of the large spread in precipitate composition observed in the previous section, a row of precipitates of the same random high-angle grain boundary was chemically analysed. Each precipitate was measured three times in order to reduce the experimental error per precipitate to 5.2%. Figs 3.3a and 3.3b depict the variation in relative solute concentrations for a row of precipitates at random high-angle grain boundaries in AA6061 and AA7050, respectively. Both alloys were artificially aged for 100 h at 160 °C. The grain boundary misorientation angles in Fig 3.3a and 3.3b are 16.6 ° and 41.2 °, respectively. Considering these figures it can be seen that, except for Zn, the measured concentrations only vary within experimental error.

3.5 Precipitation at low-angle grain boundaries in AA6061

In this section the chemical composition of precipitates at low-angle grain boundaries is investigated and compared to that of precipitates at random high-angle grain boundaries. Table 3.5 lists the relative solute concentrations of grain boundary precipitates for different low-angle boundary misorientations after 100 h of artificial ageing. The depicted values are the averages of ten precipitates per grain boundary, so that the standard deviation is 3.0%. The crystallographic structure of all of the investigated precipitates corresponds to that of the C-phase (HCP, \( a = 10.4 \text{ Å}, c = 4.1 \text{ Å} \)).

<table>
<thead>
<tr>
<th>Misorientation</th>
<th>[Mg]_{rel}</th>
<th>[Si]_{rel}</th>
<th>[Cu]_{rel}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8 ° on a [001]</td>
<td>0.73</td>
<td>0.233</td>
<td>0.033</td>
</tr>
<tr>
<td>3.3 ° on a [001]</td>
<td>0.75</td>
<td>0.214</td>
<td>0.038</td>
</tr>
<tr>
<td>11.5 ° on a [013]</td>
<td>0.74</td>
<td>0.218</td>
<td>0.044</td>
</tr>
<tr>
<td>12.8 ° on a [221]</td>
<td>0.73</td>
<td>0.234</td>
<td>0.033</td>
</tr>
</tbody>
</table>
**Fig 3.3:** Relative solute concentrations in precipitates at random high-angle grain boundaries after 100 h at 160 °C:
(a) AA6061 – Misorientation angle is 16.6 °
(b) AA7050 – Misorientation angle is 41.2 °
Based on the relative solute concentrations presented in Table 3.5, the precipitates at low-angle grain boundaries would, on average, be described by Cu$_{1.1}$Si$_{6.9}$Mg$_{22.5}$. Although the relative Mg-concentrations of the low-angle boundary precipitates are much larger than would be expected from the chemical description of the C-phase, their composition can still be compared qualitatively to that of the random high-angle boundary precipitates. When Table 3.5 is compared to Table 3.3, a significant influence of the grain boundary misorientation angle on chemical composition of the precipitates is clearly demonstrated. The relative Mg-concentration is larger for low-angle grain boundary precipitates, whereas the relative Si- and Cu-concentrations on the other hand, are smaller. As the crystallographic structure in both cases corresponds to that of the C-phase, the precipitate composition may reflect the availability of a specific solute element during its nucleation and growth, just as was observed for the grain boundary phase of Fig 3.2. A larger relative Mg-concentration therefore would suggest a larger relative grain boundary concentration of Mg in the as-quenched state. In contrast, the absolute concentrations (i.e. not relative to the other solute elements) of Mg, Si and Cu at low-angle grain boundaries are supposed to be smaller than at random high-angle grain boundaries. This argument is based on the more ‘compact’ structure for low-angle grain boundaries and thus a smaller degree of solute segregation to these boundaries. This can be attributed to the lower primary dislocation density in these boundaries, because the positions of the solute atoms were closely correlated to the cores of these primary dislocations [25].

The larger relative amount of Mg in the low-angle boundary precipitates might be explained by a site-competition effect during segregation [25], which will be more pronounced for these boundaries because of their more compact boundary structure and thus the smaller number of sites to segregate to.

Fig 3.4 depicts several low-angle grain boundaries with increasing angles of misorientation. It can be seen that below a certain angle (determined to be $\sim 2.5^\circ$), precipitation is completely absent, even after 100 h of artificial ageing. Apparently, at the smallest angles, the grain boundary structure becomes too compact for any solute segregation to occur during the water-quench, which is reflected in the absence of grain boundary precipitates even after 100 h of artificial ageing. The projected sizes of the precipitates (rod-shaped) in Figs 3.4b,c should not be compared, because the boundary planes are at different orientations with respect to the electron beam.
The compositional spread for a row of grain boundary precipitates is significantly larger for low-angle grain boundaries as can be recognized by comparing Fig 3.3a and 3.5. The smaller diffusivity of solutes at low-angle boundaries may be responsible for this, as compositional variations along the grain boundary will then be larger. Another explanation can be site selectivity, in which the extent of segregation varies markedly from one boundary site to another [25].
Fig 3.5: Relative solute concentrations in precipitates at low-angle grain boundaries in AA6061 after 100 h at 160 °C:
(a) 2.8 ° on [001]
(b) 12.8 ° on [221]
3.6 Precipitation at CSL-type grain boundaries in AA6061 and AA7050

As the atomic arrangement of CSL-type grain boundaries may influence precipitation, the effect of plane orientation of a $\Sigma 3$-boundary is studied in this section. The structure of the $\Sigma 3$-boundary is commonly reported to have a large cohesion and resistance to different kinds of embrittlement [25]. However, the grain boundary plane orientation is often neglected in these discussions, but as will be shown below, it can affect segregation and precipitation phenomena to a large degree. Fig 3.6a depicts a $\Sigma 3$-(111)/(111) grain boundary (i.e. the coherent twin boundary) in AA6061 aged for 100 h at 160 °C. As can be observed, precipitation is absent. On the contrary, extensive precipitation has occurred at the $\Sigma 3$-(100)/(221) grain boundary (i.e. asymmetrical tilt boundary) in AA7050 aged for the same time (Fig 3.6b), thereby illustrating the importance of the grain boundary plane orientation in addition to misorientation angle and axis. The different alloy composition is not believed to be of influence here. The structure of the $\Sigma 3$-(100)/(221) boundary is more open and consequently the extent of segregation and precipitation will be much larger. Comparing the precipitate size and distribution to that of precipitates at random high-angle grain boundaries, it can be concluded that the amount of segregation to both types of grain boundaries must be comparable.

Fig 3.6: Influence of plane orientation on precipitation at $\Sigma 3$ grain boundaries aged for 100 hrs at 160 °C:
(a) $\Sigma 3$ (111)/(111) GB in AA6061 – no precipitation
(b) $\Sigma 3$ (100)/(221) GB in AA7050 – extensive precipitation
In order to compare the compositional spread of precipitates at CSL-type grain boundaries to that of precipitates at random high-angle boundaries (Fig 3.3), Fig 3.7 presents the compositional spread for a row of precipitates at a $\Sigma 7$-boundary in AA6061 and the $\Sigma 3$-(100)/(221) in AA7050. The observed spread in precipitate composition (especially on the $\Sigma 7$-boundary) may be explained by an uneven segregation profile along a particular grain boundary, which may be caused by site-selectivity or a variation in plane orientation (e.g. a ledge) [26,27]. On the other hand, the average precipitate-composition at these grain boundaries, presented in Table 3.6, is comparable to that of the random high-angle boundaries in Table 3.3 and 3.4, which would imply that the free volume of these boundaries is larger than that of, for instance, the low-angle grain boundaries. The degree of segregation and precipitation may then be comparable to that of the random high-angle grain boundaries. Above results agree well with the work of Bouchet [28], where it was observed that only a few of the CSL-type grain boundaries are special regarding their degree of segregation. Negligible segregation is expected for $\Sigma 3$(111), $\Sigma 3$(211), $\Sigma 9$(221), $\Sigma 11$(311) and $\Sigma 19$ a (331), whereas a small amount of segregation is predicted for $\Sigma 5$(210), $\Sigma 5$(310), $\Sigma 27$ a (511). It can thus be concluded that the grain boundary plane, which is characterized by the interplanar spacing, is a fundamental parameter (next to the misorientation angle and axis) describing the propensity for segregation and precipitation.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>[Mg]$_{rel}$</th>
<th>[Si]$_{rel}$</th>
<th>[Cu]$_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA6061</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Sigma 7$</td>
<td>0.65</td>
<td>0.30</td>
<td>0.05</td>
</tr>
<tr>
<td>AA7050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Sigma 3$-(100)</td>
<td>0.54</td>
<td>0.39</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Fig 3.7: Relative solute concentrations in precipitates at CSL-type boundaries after 100 h at 160 °C:
(a) Σ7 in AA6061
(b) Σ3-(100)/(221) in AA7050
3.7 Matrix precipitation in AA6061

In this section, the chemical composition of the matrix precipitates is considered in order to establish a comparison to the composition of the grain boundary precipitates and to explain differences. The morphology of the matrix-precipitates was measured in the water-quenched sample aged for 100 h at 160 °C. The crystallographic structure was found to be the same as that of the grain boundary precipitates (i.e. HCP, \( a = 10.4 \, \text{Å}, \ c = 4.1 \, \text{Å} \)). The direction of length of the needle-shaped precipitates (i.e. the precipitate growth direction) was found to be parallel to the \( c \)-axis of the hexagonal unit cell. As the matrix precipitates are small with respect to the minimum electron probe size, the chemical composition was measured when the needles were oriented parallel to the electron beam in order to obtain a maximum yield of X-rays originating from the precipitate.

Fig 3.8 depicts the spread in relative concentrations of Mg, Si and Cu for several precipitates within one grain. As can be observed, the spread is much more pronounced compared to that of the grain boundary precipitates, which may be explained by the much larger solute diffusivity at the grain boundary, so that compositional differences can be balanced more easily.

![Fig 3.8: Relative solute concentrations for matrix precipitates in AA6061 after 100 h at 160 °C.](image-url)
In Table 3.7 the average relative concentrations of these elements are presented. When comparing these values to those of the grain boundary precipitates (Table 3.3 and 3.5), it can be seen that especially the relative concentration of Mg is significantly larger for the grain boundary precipitates. This may be interpreted as additional support for the idea that Mg is favoured in a competition for sites at the grain boundaries. Based on the values listed in Table 3.7, the matrix precipitates in AA6061 may be described by $\text{Cu}_{1.5}\text{Si}_{6.5}\text{Mg}_{12.7}\text{Al}_{0.3}$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.61</td>
</tr>
<tr>
<td>Si</td>
<td>0.32</td>
</tr>
<tr>
<td>Cu</td>
<td>0.07</td>
</tr>
</tbody>
</table>

### 3.8 Grain Boundary Precipitate – Matrix Orientation Relation and Precipitate Growth Direction in AA6061

Fig 3.9 shows selected-area electron diffraction (SAED) patterns of the grain boundary precipitate with the Al-matrix in [010]- and [001]-projection. As mentioned earlier, the crystallographic structure of the grain boundary precipitates is hexagonal-close-packed with $a = 10.4$ Å and $c = 4.05$ Å. From Fig 3.9a, it can be derived that the [001]-axis of the grain boundary precipitate is parallel to the [001]-axis of the Al-matrix. Furthermore, from Fig 3.9b a rotation about the [001]-axis of $11.3^\circ$ is measured between the precipitate $(1\overline{1}0)$-planes and the matrix (010)-planes. This angle also is exactly equal to the angle between the (010)- and (150)-planes of the Al-matrix, so that the orientation relation can be expressed as: [001]$_C$ // [001]$_{Al}$ and (110)$_C$ // (150)$_{Al}$ which is equivalent to: [001]$_C$ // [001]$_{Al}$ and (210)$_C$ // (100)$_{Al}$ (i.e. the orientation relation reported in literature).

From Fig 3.10, in which a high-resolution image of the precipitate-matrix interface is depicted along the [001]$_C$ and [001]$_{Al}$ projections, the $(5\overline{1}0)_{Al}$-plane can be observed to be the habit plane of the precipitate.
**Fig 3.9:** SAED-patterns of grain boundary precipitate and matrix (encircled spots) in AA6061: (a) in [010]-matrix projection   (b) in [001]-matrix projection

**Fig 3.10:** High resolution TEM image of interface between grain boundary precipitate (C-phase) and matrix in AA6061. Positions of atom columns in C-phase are represented by white dots.
The grain boundary precipitate growth direction can be derived from Fig 3.11, in which two different two-dimensional projections of the same row of grain boundary precipitates are depicted. Fig 3.11a shows a bright-field image of precipitates projected along the [001]_C-axis and simultaneously, one of the matrix grains projected along the [001]_Al-axis. At this point, the projected size of the precipitate is smallest. Fig 3.11b depicts the grain boundary precipitates when the matrix grain is tilted from its [001]_Al- to its [011]_Al-projection (i.e. 45°-rotation about the [100]_Al-axis). The projected size of the grain boundary precipitates is larger now. From the above observations it can be concluded that the growth direction of the grain boundary precipitates is along the [001]_C-direction. This result will be used in Chapter 4, where grain boundary precipitation is modelled.

For the other, much smaller, class of grain boundary precipitates in AA6061 also a hexagonal structure was determined. For these precipitates, the lattice parameters \( a = 7.05 \text{ Å} \) and \( c = 4.05 \text{ Å} \), the orientation relationship \([001]_\beta'// [001]_\text{Al} \) and \((100)_{\beta'}// (100)_{\text{Al}}\) and the growth direction \([001]_{\beta'}\) all corresponded closely to those of the \(\beta'\)-phase.
The orientation relationship between grain boundary precipitates (C-phase) and the matrix observed in AA6061 can be rationalized on the basis of a good fit of lattice spacing. The perfect match of lattice planes in one direction, as depicted in Fig 3.12a, is what gives rise to the long dimension of the lath parallel to the $<001>_{\text{Al}}$-directions. The repeat distance along the $<150>_{\text{Al}}$-direction is $(4.04\sqrt{26})/2 = 10.3$ Å. This is nearly the same as the lattice parameter ($a = 10.4$ Å) of the grain boundary precipitate (Fig 3.12b). Hence, during solid-state precipitation, the grain boundary precipitate minimizes its interfacial free energy by maximizing its area on the $\{150\}_\text{Al}$-planes (i.e. the habit plane of Fig 3.10). Overall, the precipitate is rod-shaped with the [001]-direction as its growth direction, which was also determined experimentally.

The orientation relationship between the $\beta'$-phase and the Al-matrix can also be understood on the basis of the two unit cells of precipitate and matrix. Again, the $c$-parameter of the precipitate hexagonal unit cell is equal to the lattice parameter of Al (Fig 3.12a). The [001]-projection of the observed orientation relation between $\beta'$ and the Al-matrix is depicted in Fig 3.12c. The parallelism between $(100)_{\text{Al}}$ and $(100)_{\beta'}$ can be seen as a rotation over $30^\circ$ between $(010)_{\text{Al}}$ and $(1\overline{1}0)_{\beta'}$. By this rotation, a fit of 3 $\beta'$-atoms to 4 Al-atoms is realized and a relatively low interfacial energy is obtained.

One of the reasons that a metastable phase forms prior to an equilibrium phase during precipitation is its lower interfacial energy. Although equilibrium phases have the largest volume free energy $\Delta G_v$, their interfacial energy term $\gamma_{\alpha\beta}$ usually is larger than that of metastable phases, because in general they cannot form in low interfacial energy configurations with the matrix. Because the term $\gamma_{\alpha\beta}$ is cubed in the expression for the nucleation barrier $\Delta G^*$ (equation (4.9), Chapter 4), formation of the equilibrium phase is usually more difficult than that of competing metastable phases. However, the C-phase is an exception, because although it is an equilibrium phase (high $\Delta G_v$), it also can form in a low-energy configuration as explained above. Hence, its interfacial energy term $\gamma_{\alpha\beta}$ is low and the entire expression for the nucleation-barrier is low, giving rise to preferred nucleation of this phase compared to competing phases. The time needed to achieve steady-state nucleation (equation (4.12), Chapter 4) is significantly smaller as well. This may explain the larger amount of C-phase observed with respect to $\beta'$ (small $\gamma_{\alpha\beta}$, but not an equilibrium phase and therefore small $\Delta G_v$). Consequently, the C-phase might very well be nucleated directly at the start of ageing without any precursors.
**Fig 3.12a:** Unit cells of Al, C-phase and β'-phase.

**Fig 3.12b:**
Explanation of 11.3° - rotation between (010)$_{Al}$ and (110)$_{C}$ on an atomic scale.

**Fig 3.12c:**
Explanation of 30°-rotation between (010)$_{Al}$ and (110)$_{β'}$ on an atomic scale.
The ability for a precipitate to form low energy interfaces with both adjacent grains is affected by the grain boundary misorientation. This only happens for special cases and most of the times the facet will be established with respect to only one of the matrix grains [29].

Because of the shape and habit plane of the C-phase precipitate, it can have in total twelve orientation-variants in the Al-matrix. A moving dislocation, therefore, sees a different configuration of strain fields and precipitate morphologies in front of it. It is suspected that this may be one of the causes of the increase in strength of the Al-Mg-Si alloys with Cu additions.

### 3.9 Grain boundary precipitate – matrix orientation relation and precipitate growth direction in AA7050

As mentioned in section 3.4.1, the crystallographic structure of the grain boundary precipitates in AA7050 after 5 h of ageing was found to be hexagonal with \( a = 5.1 \text{ Å} \) and \( c = 8.6 \text{ Å} \). Fig 3.13 presents the selected-area electron diffraction (SAED) patterns from which the grain boundary precipitate-matrix orientation relationship can be expressed as: \( [001]_\eta // [\overline{1}11]_{\text{Al}} \) and \( (\overline{1}00)_\eta // (\overline{1}10)_{\text{Al}} \). This relationship corresponds to that reported in literature and can be interpreted as an indication that \( \eta \) was formed from \( \eta' \), which was also reflected in a different crystal structure (i.e. that of the \( \eta' \)-phase) for the first stages of ageing.

![Fig 3.13: SAED-patterns of grain boundary precipitate and matrix (encircled spots) in AA7050: (a) in [112]-matrix projection (b) in [001]-matrix projection](image)
The orientation relation between the grain boundary precipitates and the matrix in AA7050 can be rationalized on the basis of plane spacing. The spacing of the $(100)_{\eta}$-planes is 4.5 Å, whereas the spacing of the $(220)_{Al}$-planes is 1.43 Å. The precipitate is oriented such that about three $(220)$-matrix plane-distances fit to one $(100)$-plane distance of the precipitate. In contrast to the grain boundary precipitates in AA6061, the precipitates in AA7050 seem to comply with the reported matrix precipitation sequence. The composition, however, is different from that of the $\eta$-phase, because Zn is partially substituted by Cu and Al. Although formation of low-energy facets may be plausible according to the observed crystallographic orientation relationship, one specific growth direction for the grain boundary precipitates in AA7050 could not be found.

3.10 DISCUSSION & CONCLUSIONS

Two different phases were found to nucleate at the grain boundaries of AA6061, which are the $\beta'$- and the C-phase. The extent of precipitation of the latter phase is much larger, which could be explained on the basis of its smaller nucleation-barrier and -time. This argument may also explain why the C-phase is already present after ageing for 0.5 h and thus is most probably the nucleation phase. In addition, the grain boundary precipitate growth direction in AA6061 (i.e. $[001]_{Al}$) can be understood on the basis of minimization of the interfacial energy term. For AA7050, the $\eta'$-phase is found at the grain boundaries during the first stages of ageing. Further ageing will result in transformation to the $\eta$-phase. Although no specific growth direction was found, formation of low-energy facets may be plausible for the latter.

For both AA6061 and AA7050, the crystallographic orientation relation between the matrix and the grain boundary precipitates is corresponding to that reported for the matrix precipitates [11,23].
The relative concentrations of solute elements in the grain boundary precipitates reflect their availability (or supply) during precipitate growth. This can be inferred from:

- *Changes in chemical composition during artificial ageing whereas the structure remains unchanged.*
- *A variable chemical composition within one large grain boundary phase, which has the same overall structure (air-cooled sample)*
- *Large compositional differences between the precipitates at the grain boundary and in the matrix, for an unaltered structure.*

The ability of atoms in the C-phase to interchange (i.e. Mg and Al vs. Cu and Si) renders this precipitate a suitable indicator to reflect variations in solute concentrations during nucleation and growth.

The measured relative Mg-concentration of the precipitates in AA6061 is on average 0.655 for the random high-angle grain boundaries and 0.738 for the low-angle grain boundaries. For the matrix precipitates the value is 0.613, which is below the maximum value (i.e. 0.619 when all Al is replaced by Mg) based on the reported chemical description of the C-phase [11]. Probably, the relative concentrations of the solute elements at nucleation and growth are different at the grain boundary, which is reflected in a different precipitate composition. At the grain boundaries of AA6061, a site-competition effect between Mg, Si and Cu may be prevalent, in which Mg may be favoured. This can be understood because larger atoms generally have higher distortion energies in the matrix. As the atomic radius of Mg (1.50 Å) is larger than that of Si (1.11 Å) and Cu (1.40 Å) [30-32], it may explain the higher relative content of Mg in the grain boundary precipitates. This point will be further elaborated and discussed in Chapter 4. The site-competition effect is amplified at low-angle boundaries. Because of the more compact structure of these boundaries, the amount of segregation is smaller and thus effects of site-competition may become more prevalent.
For the CSL-boundaries investigated in this work, the effects of site-competition are not as large as for the low-angle boundaries. On the other hand, the spread in composition along a row of precipitates is pronounced. Although the importance of the grain boundary plane orientation on precipitation behaviour was stressed for the Σ3-boundary (e.g. no precipitation at the coherent twin boundary), the excess volume of most of the CSL-boundaries may be significantly larger than that of the low-angle grain boundaries so that the degrees of segregation and precipitation are comparable to that of the random high-angle grain boundaries. This is also reflected in the average relative solute fractions in the precipitates. The observed spread in precipitate composition (especially on the Σ7-boundary) may be explained by an uneven segregation profile along a particular grain boundary, which may be caused by a variation in the plane orientation or by grain boundary site-selectivity of the solute elements.

The spread in the composition of the matrix precipitates in AA6061 is pronounced. This can be understood, because the diffusivity of the matrix is much lower than that of the grain boundaries. Consequently, compositional variations will be larger.

From the previous discussion, the conclusion can be drawn that the C-phase can exist with a broad range in relative Mg- and Si- and Cu-concentrations. The ability for Al to interchange with Mg atoms and Cu to interchange with Si atoms in the C-phase is pointed out by Arnberg and Aurivilius [16]. However, as the relative concentration of Mg is in most cases larger than 0.62, other chemical descriptions, which have not been reported yet, may be valid for the grain boundary precipitates. In addition, fluorescence of Mg by X-rays of Al should also be considered possible in this discussion.

The crystallographic structure of grain boundary precipitates together with their chemical composition yield a better understanding of their growth mechanism (e.g. presence of low-energy facets and concentration of the rate-controlling element) and thus provide a clue with respect to the strength of the grain boundary as a function of heat treatment. Results from this chapter will be used in Chapter 4, where grain boundary segregation during quenching and grain boundary precipitation during artificial ageing will be modelled.
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Chapter 3