Grain boundary phenomena and failure of aluminium alloys

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Chapter 2

BASIC CONCEPTS

2.1 INTRODUCTION

Because the range of chemical compositions of aluminium alloys is rather broad, first an introduction into the different classes of aluminium alloys will be presented. Of those, the alloys investigated in this thesis are characterized by composition and their industrial processing routes are described. Subsequently, the basic types of grain boundaries will be considered. Because Chapters 5 and 6 of this thesis are predominantly based on mechanical testing of aluminium alloys, tensile testing and the mechanisms of fracture that may be prevalent, are elaborated.

In the second part of this chapter the experimental techniques are described. This part contains a brief description of the analytical transmission electron microscope, in which quantitative X-ray microanalysis plays a dominant role. In addition, determination of specimen thickness and TEM-sample preparation will be described. Finally, a method is given to resolve the grain boundary geometry in a transmission electron microscope.

2.2 WROUGHT ALUMINIUM ALLOYS

The Aluminium Association alloy designation system for wrought alloys begins with “AA” followed by a four-digit number system, where the first of the four digits in the designation indicates the alloy group. The various wrought alloys can most readily be described by adopting two basic groups, being the non heat-treatable and the heat-treatable alloys.
Non heat-treatable alloys obtain higher strength either by strain-hardening (e.g. cold working) or by solid solution. They include the pure aluminium group (1XXX), the Al-Mn group (3XXX), the Al-Si group (4XXX) and the Al-Mg group (5XXX). These alloys are mostly used for flat products such as plate, thin sheet and foils. To some extent, extrusions from the 1XXX- and 5XXX-groups can be found. Plate and sheet are often delivered in cold-rolled tempers for high strength applications, but the best formability is in the soft annealed temper. Very good forming properties are often required from extruded products made of these alloys, while high strength is less important. Therefore, the extrusions are often delivered in annealed or as-fabricated condition.

Heat-treatable alloys can achieve a higher strength by heat-treatment and therefore they contain one or more elements chosen to obtain this higher strength by precipitation hardening during artificial ageing. These alloys include the Al-Cu-(Mg) (2XXX), Al-(Cu)-Mg-Si (6XXX) and Al-(Cu)-Mg-Zn (7XXX)-groups. The 2XXX-group contains alloys with copper as the prime hardening element. Often magnesium is added to increase the maximum strength. These alloys obtain their very high strength by precipitation of the phases CuAl$_2$ and/or CuMgAl$_2$. Alloys from this group are characterised by high strength, poor corrosion resistance, very low extrudability and weldability. They are widely used in aviation- and space industry, but also as machine parts, bolts and rivets.

The 6XXX-group contains magnesium and silicon additions and sometimes small amounts of copper, chromium or manganese. The alloys are reported to obtain increased levels of strength by precipitation of Mg$_2$Si-precipitates and their mechanical properties range from "soft" to those of structural steel. The extrudability is generally very good, the alloys are weldable and have a good corrosion resistance (for some alloys even in marine atmospheres) [1], they are well suitable for most of the common surface treatment processes (anodising, chromating, phosphating, painting, plating etc.) and they have good strength properties to above 100 °C. Typical applications range from window frames to heavily loaded structures. Approximately 80 % of the annual world production of extrusions exists of alloys from this group.

The 7XXX-group contains high-strength materials similar to Al-Cu-(Mg), but with zinc instead of copper as the main alloying element. However, copper can also be added in smaller amounts. The high strength is due to precipitation of
MgZn\textsubscript{2}-precipitates. The alloys without copper have a tensile strength somewhat above the strongest of the 6XXX-alloys, but their extrudability is slightly worse. On the other hand, they are much less quench-sensitive and can be air cooled for much greater wall thickness. Alloys containing copper attain the highest strength of all aluminium alloys, exceeding normal structural steel. The extrudability is very poor and the alloys are not weldable under normal conditions. Al-Mg-Zn-alloys are mostly used for structural applications in the automotive industry where high mechanical strength is needed. Al-Cu-Mg-Zn alloys on the other hand, are used for particularly high stressed components in the aviation- and space industry.

In this thesis, particular alloys of the 6XXX- and 7XXX-series are considered. For grain boundary segregation and precipitation studies during quenching and artificial ageing procedures, AA6061 and AA7050 are used. In order to investigate the effects of heavy metal impurities like lead and bismuth on dynamic- and liquid-phase embrittlement, the AA6262 alloy is explored. The chemical compositions [2] of these alloys are listed in Table 2.1.

**Table 2.1: Compositional ranges of the alloys studied in this thesis**

<table>
<thead>
<tr>
<th>Element</th>
<th>Conc. (at%) AA6061</th>
<th>Conc. (at%) AA6262</th>
<th>Conc. (at%) AA7050</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.8-1.2</td>
<td>0.8-1.2</td>
<td>1.9-2.7</td>
</tr>
<tr>
<td>Si</td>
<td>0.4-0.8</td>
<td>0.4-0.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Ti</td>
<td>0.15</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>Cr</td>
<td>0.04-0.35</td>
<td>0.04-0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>Mn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe</td>
<td>0.7</td>
<td>0.7</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu</td>
<td>0.15-0.40</td>
<td>0.15-0.40</td>
<td>2.0-2.6</td>
</tr>
<tr>
<td>Zn</td>
<td>0.25</td>
<td>0.25</td>
<td>5.7-6.7</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0002</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>Bi</td>
<td>0.0008</td>
<td>0.07</td>
<td>-</td>
</tr>
</tbody>
</table>

From the as-cast state, the alloys are homogenised in order to enhance the overall extrudability. The next steps of the industrial processing route for precipitation-strengthened alloys are schematically presented in Fig 2.1.
Heat treatable alloys are typified by a marked increase in solubility of the major alloying element with increasing temperature. Therefore, the first stage of any heat treatment must be to form a solid solution by soaking the material at a temperature above the solvus, but below the solidus to avoid incipient melting. Subsequently, the alloy must be cooled so rapidly that precipitation will be avoided and the solute maintained in a supersaturated solid solution. Finally, the alloy is artificially aged for a period at a temperature below about 180 °C, which induces nucleation and growth of the strengthening precipitates. Most of the 6XXX-series alloys are quenched immediately after extrusion followed by an artificial ageing sequence (Fig 2.1a), whereas the 2XXX- and 7XXX-series alloys are solution heat treated in a separate operation and artificially aged afterwards (Fig 2.1b) [2].

**Fig 2.1:** Industrial processing routes of aluminium alloys:
2.3 COOLING RATES IN WATER OR STILL AIR

The instantaneous temperature of samples cooled in water or still air, is described by

\[
\frac{T - T_{\text{med}}}{T_i - T_{\text{med}}} = \exp \left[ -\frac{t}{\tau_a} \right]
\]

where \( \tau_a = \frac{\rho C_p V}{A_s h} \) (2.1)

Here, \( T \) is the temperature at time \( t \), \( T_i \) is the initial temperature (i.e. the temperature of solution heat treatment), \( T_{\text{med}} \) is the temperature of the cooling medium, \( \rho \) is the density, \( C_p \) the specific heat, \( V \) the volume and \( A_s \) the surface area of the medium that is cooled. For water and still air, the heat transfer coefficients \( h \) are 2-40 kW m\(^{-2}\) °K\(^{-1}\) and 10 W m\(^{-2}\) °K\(^{-1}\), respectively [2].

2.4 GRAIN BOUNDARIES

Crystalline solids usually consist of a large number of randomly oriented grains (single crystals) separated by grain boundaries. The geometry of a general grain boundary is characterized by five geometric parameters; three angles characterize the crystallographic orientation relationship between the two grains and two angles describe the boundary inclination (i.e. the orientation of the grain boundary plane with respect to the two adjacent crystals). These five parameters are sufficient to characterize the boundary macroscopically, but in order to describe the atomic arrangement in a boundary, three more parameters are required due to the relaxation of the atoms at the boundary [3].

It is generally accepted that the energy of a grain boundary originates from the fact that the atoms at the boundary are removed from the positions they would occupy in a perfect crystal lattice. Therefore, the energy of a grain boundary essentially represents the distortion of the crystal lattice at the boundary or the misfit of the atoms of both grain lattices in the boundary region. The average distance between the atoms of a grain boundary is larger than in an ideal crystal and therefore the consequent displaced positive charge of the atom cores has to be screened by a redistribution of the conduction electrons. The increase in energy due to this redistribution is assumed to be equal to the grain boundary energy.
Various degrees of misalignment between adjacent grains are possible. When the misorientation between the grains is small, the boundary consists of an array of dislocations and is called a low-angle boundary (Fig 2.2). Frequently, regions of material separated by low-angle grain boundaries are termed subgrains. When the misorientation becomes larger, the atomic arrangement at the boundary is more complicated and varies significantly with the angle of misorientation.

2.4.1 Low-angle grain boundaries

Experiments have been mostly carried out on the tilt boundaries. The initial increase in the grain boundary energy at small tilt angles may be explained by the Read-Shockley equation of the well-established dislocation model of low-angle grain boundaries [4]

\[ E = E_0 \theta (A - \ln \theta) \]  

(2.2)

Here \( E_0 \) is a constant, which depends on the elastic properties of the material and \( A \) is a constant, which depends on the core energy of an individual dislocation. \( \theta \) is the misorientation angle difference between the two grains. The Read-Shockley equation is derived by integrating the elastic energy density of a network of non-interacting dislocations from the core radius to a distance of the order \( b/2\theta \) (\( b \) is the magnitude of the Burgers vector).
It is expected that this approximation will become invalid when \( b/2\theta \) is in the order of the core radius, because at this point the larger part of the strain energy resides in regions near the dislocation core where the assumed linear stress-strain relationship is not valid.

Although high-angle boundaries can be described in principle by arrays of crystal dislocations, this model has little physical significance. For this type of grain boundaries a different reference lattice can be employed, which will be discussed in the next section.

2.4.2 Coincident site lattice (CSL) grain boundaries

The misorientations of grain boundaries in cubic metals are often observed to be close to special orientation relationships that belong to a class known as coincident site lattice (CSL) orientations. A CSL-boundary can be considered in the following way: If two identical, but misoriented, cubic lattices are allowed to interpenetrate, then for particular misorientations of these lattices, there will be a number of sites in the interpenetrating lattices which are common to both of the individual lattices. A particular CSL-boundary is specified by an odd integer \( \Sigma \), where \( 1/\Sigma \) is the fraction of lattice sites that are common to both lattices. An example of a CSL-boundary is given in Fig 2.3 (taken from [5]), which is a [001]-projection showing the atomic arrangement of a \( \Sigma 5 \)-boundary formed by two FCC lattices misoriented by a rotation \( \theta = 36.87^\circ \) around a common axis \( \mathbf{u} = [001] \). Lattice 1 is represented by the symbols + and \( \square \), where + is in the plane of the page and \( \square \) is \( \frac{1}{2}[001] \) above the plane of the page.

*Fig 2.3: Schematic representation of a \( \Sigma 5 \)-boundary in [001]-projection.*
Similarly, lattice 2 is represented by the symbols $\times$ and $\diamond$, where $\times$ is the plane of the page and $\diamond$ is $\frac{1}{2}[001]$ above the plane of the page. The coincident sites are designated by coincident symbols $\ast$ and four of these in the plane of the page, are linked by dashed lines. For values of $\Sigma$ larger than 11, more than one CSL can exist for a given value of $\Sigma$, and these involve non-equivalent values for $u$ and $\theta$. These are distinguished by subscripts $a$ and $b$, where $a$ is given to the smallest angle of misorientation.

The observed energy curve for high-angle grain boundaries exhibits cusps for the inclinations that allow the best atomic fit in the boundary (i.e. at the misorientation angles of the CSL boundaries). This is depicted in Fig 2.4 (taken from [6]), which shows measured relative grain boundary energies for symmetric tilt boundaries by rotation about a $<110>$-axis in aluminium. The width of the observed cusps suggests that when the orientation relationship deviates from the ideal coincidence relationship, the structure of the coincidence boundary is not immediately lost and a torque will act on the grain boundary [7].

![Fig 2.4: Measured relative grain boundary energy vs. angle of symmetric tilt boundaries in aluminium. The rotation axis is parallel to $<110>$.](image)

To assess whether a grain boundary belongs to a particular CSL configuration, the Brandon Criterion [8,9] was proposed to determine the maximum allowable angle deviation $\Delta \theta$

$$\Delta \theta < \frac{15^\circ}{\sqrt{\Sigma}}$$  \hspace{1cm} (2.3)
From now on, grain boundaries with misorientation angles that do not correspond within the limits of the Brandon criterion to those of CSL-boundaries with $\Sigma < 29$, will be termed "random high-angle" or "general" grain boundaries.

Of the whole boundary population, the only CSL-boundaries reported to have predominantly special geometries are the $\Sigma 3$ and the $\Sigma 9$ [10]. Although many of the reported investigations indicate that there is some relationship between CSL-fraction and a particular property, the correlation is certainly not universal [11,12]. In this respect, it is important to have a knowledge of the grain boundary plane-crystallography [7,13] in addition to its misorientation angle and axis, because the free volume and hence the properties of grain boundaries may be inferred from the boundary-plane type. Many CSL-boundaries, almost all having $\Sigma > 3$, do not have a straight planar trace, which means that the boundary plane crystallography is varying. For a boundary that belongs to $\Sigma 3$ according to misorientation angle and axis, different configurations are thus still possible based on the orientation of the boundary plane. Of the lowest energy are the tilt boundaries on the $<011>$-axis [12]. These include the symmetrical twin grain boundaries $(111)/(111)$ (coherent twin) and $(211)/(211)$ (incoherent twin). Asymmetrical twin grain boundaries on the $<011>$-axis possess a slightly larger energy. Other tilt or twist boundaries (not on the $<011>$-axis) are also possible. Of the largest energy within the $\Sigma 3$-group, are the boundaries having an irrational plane.

2.4.3 Grain boundary cohesive strength versus chemistry

Many metals, which fracture in either a transgranular brittle mode or in a ductile mode, are found to fracture in an intergranular mode when they contain a dilute bulk-concentration of substitutional solute atoms of a type, which segregates strongly to the grain boundaries. This may be attributed to a relatively large decrease in the quantity $2\gamma_b - \gamma_{gb}$ relative to $2\gamma_{sl}$. Here $\gamma_b$ is the energy of the free surface produced by boundary fracture, $\gamma_{gb}$ is the grain boundary energy and $\gamma_{sl}$ is the corresponding energy produced by lattice fracture. The fracture mode depends upon both the degree of segregation to the different boundaries and upon the geometry of the slip systems that are available to generate shielding dislocations.
Segregated atoms thus change the energy of a grain boundary and it can intuitively be understood that strong segregates increase the grain boundary energy strongly. However, an increase in energy does not yet mean a reduction of the cohesive strength. In fact, some segregated atoms, like boron in steels, strengthen the grain boundaries, whereas others like sulphur and phosphorus weaken them. Both the increase of grain boundary energy and the reduction of surface free energy determine whether the boundary is a preferential path for crack propagation. Thus, an impurity atom that prefers to reside on a free surface rather than on a grain boundary reduces the cohesive strength, since separation of the grains leads to a favourable location of the impurity atom. A number of studies have shown that the degree of embrittlement depends upon the boundary type. It is noted that small-angle boundaries (which always possess relatively low energies and degrees of segregation) are highly resistant to intergranular fracture [18].

2.5 TENSILE TESTING AND FRACTOGRAPHIC ANALYSIS

All tensile tests presented in this thesis are performed using a tensile substage that fits into an environmental scanning electron microscope (Fig 2.5). With this stage, elongation rates in the range 0.2 - 25 µm s\(^{-1}\) can be applied. Simultaneously, the sample can be heated up to temperatures of 1000 °C.

\textit{Fig 2.5:}
\textit{Tensile substage.}
2.5.1 Modes of fracture

A fracture surface is one of the most important sources of information revealing the cause of failure. The principal technique used to analyse it is electron fractography, mostly performed in a scanning electron microscope. For a given material, the fracture mechanism depends on temperature, stress, loading rate, stress-triaxiality and the chemical environment [14,15]. This has been illustrated for aluminium by Ashby [16,17] in the form of fracture mechanism maps, which are schematically depicted in Fig 2.6.

![Fracture mechanism maps: (a) High purity aluminium (b) Aluminium alloy](image)

Additional microstructural parameters that govern the fracture mode for a given polycrystalline material are: the types of grain boundaries present, the presence of solute atoms that may segregate strongly to these grain boundaries and the presence of second phase particles [18].

The principal fracture modes, of which there are essentially four, are: cleavage, dimple rupture, decohesive rupture and fatigue [14]. The first three will be briefly discussed in this section. For either mode, fracture can occur either along a transgranular (through the grain) or along an intergranular (via the grain boundary) fracture path.
Cleavage

Cleavage is low-energy fracture that propagates along low-index crystallographic planes, by forces that are large enough to rupture the atomic bonds. Theoretically such planes would be completely flat and featureless, but in practice grain boundaries, inclusions and other imperfections will induce certain irregularities in the cleavage plane. This mode leads to fracture surfaces that are macroscopically oriented normal to the applied tensile stress. On a microscopic level however, the fracture path follows the possible cleavage planes or grain boundaries. The cleavage fracture stress depends on temperature, strain rate and degree of stress triaxiality. This fracture mode is frequent in body-centred cubic and hexagonal systems, but nearly never occurs in face-centred-cubic materials. The decrease in flow stress with increasing temperature, which is typical for FCC-materials, favours fracture by ductile void growth and coalescence and makes cleavage less likely.

Dimple-rupture or microvoid coalescence

When an alloy is subjected to mechanical overload, it may fail by a process called microvoid coalescence. Voids nucleate at regions of localized strain discontinuity, mostly associated with second phase particles, inclusions, grain boundaries and dislocation pile-ups. With increasing strain, the microvoids grow, coalesce and eventually form a continuous fracture surface, which is characterized by numerous cuplike depressions, also referred to as dimples. Depending on whether the alloy fails along a grain boundary or through the grain, this fracture mode can be classified as intergranular microvoid coalescence or transgranular microvoid coalescence, respectively. Exposed surfaces that are the result of shear-fracture generally exhibit elongated dimples with relatively flat regions in between [19,20].

Decohesive rupture

This type of fracture is generally the result of a reactive environment or a unique microstructure and is most often associated with low-ductility intergranular fracture. The grain boundaries are easy sites for segregation as well as penetration routes for low melting point metals. The presence of these constituents at the boundary can significantly reduce its cohesive strength and promotes decohesive fracture.
Fracture of weak grain boundary films, rupture of melted and resolidified grain boundary constituents (as in overheated aluminium alloys) or separation of melted material in the grain boundary (i.e. liquid phase embrittlement) can produce decohesive rupture.

Creep-rupture is time-dependent failure that results when a metal is subjected to stress and elevated temperature (40-70 % of the absolute melting temperature) for extended periods. The common cause for most of these problems is the increasing mobility of atoms by diffusion at higher temperatures. Mostly, creep-ruptures exhibit an intergranular fracture surface; transgranular creep-ruptures result from high applied stresses (higher strain rates) and fail by a void-forming process similar to that of microvoid coalescence. As shown in Fig 2.7 (taken from [15]), intergranular creep-ruptures can occur by either triple point cracking (wedge-cracks) or grain boundary cavitation, determined by the strain rate and temperature. The first mechanism (Fig 2.7a) prevails under conditions of relatively high strain rates and intermediate temperature. There may be other cases, in which wedge-cracking occurs by brittle decohesion of the grains assisted by segregated impurity atoms. At higher temperatures and lower strain rates, grain boundary sliding favours cavity formation (Fig 2.7b). A combination of the two mechanisms is possible as well. The grain boundary cavities should not be confused with microvoids formed in dimple-rupture. There is a fundamental difference between them; the cavities are formed during a diffusion-controlled process, while microvoids are the result of complex slip.

![Fig 2.7: Creep-ruptures by: (a) brittle decohesion (b) cavity coalescence](image)
2.6 Analytical Transmission Electron Microscopy

Today, transmission electron microscopes (TEM) constitute the most dedicated tools for the characterization of materials. Image formation in the electron microscope involves the use of electromagnetic lenses so that there are rotations of ray paths due to the magnetic fields of the lenses, in addition to the inversions due to crossing ray paths common to optical microscopes. Usually such rotations and inversions must be determined in order to relate crystallographic directions in a diffraction pattern to directions in the corresponding image. For the JEOL-2010F analytical transmission electron microscope used in this work, however, these rotations are absent so that the diffraction pattern can be related directly to the corresponding image. In addition to TEM-mode (parallel incidence of the electron beam), this microscope can also be operated in energy-dispersive-spectroscopy (EDS) and nano-beam-diffraction (NBD) mode (Fig 2.8). In the EDS-mode the electron beam is incident at larger $\alpha$-angles, whereas for the NBD-mode these angles are smaller. In these latter modes, the diameter of the electron beam can be reduced to ~ 0.5 nm, thus enabling very localized chemical and structural analysis.

![Fig 2.8: Different operational modes of JEOL-2010F analytical microscope.](image)
2.6.1 Quantitative X-ray microanalysis

Electrons are one type of ionising radiation, which is the general term given to radiation that is capable of removing one of the tightly bound inner-shell electrons from the attractive field of the nucleus. One of the advantages of using this type of radiation is that it produces a wide range of secondary signals from the specimen, like secondary electrons, backscattered electrons, Auger electrons and X-rays. In analytical transmission electron microscopy, the X-rays play a dominant role in both qualitative and quantitative chemical analysis of the material.

The accelerated electrons ionise the atoms in the sample, which then emit characteristic X-rays. Because the electrons are also slowed down by the interaction with the nuclei of the atoms, they produce a continuum of Bremsstrahlung X-rays. The result is that the characteristic X-rays appear as Gaussian-shaped peaks superimposed on a background of the Bremsstrahlung X-rays. The interface between the microscope and the XEDS-detector is given in Fig 2.9. A super ultra thin window (SUTW) is mounted in front of the Si-detector, which has the advantage that X-rays from elements as light as boron can be detected.

**Fig 2.9:** Interface between XEDS detector and transmission electron microscope.
The three main parts of the XEDS-part are the Si-detector, the processing electronics and the multi-channel-analyser display (MCA). The Si-detector generates a charge pulse proportional to the X-ray energy that is converted to a voltage. This signal is subsequently amplified through a field-effect transistor, isolated from other pulses, further amplified and identified. Finally, a digitised signal is stored in a channel assigned to that energy in the MCA.

The concentrations in weight percent of each element A and B can be related to their respective intensities \( I \) in the X-ray spectrum by using the Cliff-Lorimer equation\[21\]

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]

(2.4)

The term \( k_{AB} \) is actually not a constant and \( k_{AB} \)-factors can only be compared when they are obtained under identical conditions, e.g. same accelerating voltage, same detector configuration and same peak-integration and background-subtraction routines. Table 2.2 lists the \( k_{ASi} \)-values of different elements using a 200 kV electron beam and a Si-detector. Nowadays, the steps for obtaining the quantification of an X-ray spectrum are almost fully automated using the MCA system. The intensities \( I_A \) and \( I_B \) are measured, their background is subtracted and they are integrated. For quantification, K\(\alpha\)-lines are most suitable. Use of L- or M-lines is more difficult, because of the many overlapping lines in each family, but may be unavoidable if the K\(\alpha\) lines are too energetic (> 20 keV) and consequently pass through the 3 mm Si-detector.

**Table 2.2: \( k_{ASi} \)-values for different elements [22]**

<table>
<thead>
<tr>
<th>Radiation</th>
<th>( k_{ASi} (200 \text{ keV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg K(\alpha)</td>
<td>1.81 ± 0.18</td>
</tr>
<tr>
<td>Al K(\alpha)</td>
<td>1.25 ± 0.16</td>
</tr>
<tr>
<td>Si K(\alpha)</td>
<td>1.00</td>
</tr>
<tr>
<td>Cu K(\alpha)</td>
<td>1.51 ± 0.40</td>
</tr>
<tr>
<td>Zn K(\alpha)</td>
<td>1.63 ± 0.28</td>
</tr>
<tr>
<td>Pb L(\alpha)</td>
<td>6.5</td>
</tr>
<tr>
<td>Bi L(\alpha)</td>
<td>6.6</td>
</tr>
</tbody>
</table>
An unfortunate aspect of the Cliff-Lorimer equation for thin foil analysis is the relatively large error that may be associated with it. Poor counting statistics (because of the thin foil) may sometimes be a source of error in the quantification. As the JEOL-2010F TEM is equipped with a high-intensity field-emission gun, these effects can be reduced. A further decrease in error can be accomplished by using longer acquisition times, but this may have the drawback of contamination and specimen drift. The latter is extremely disadvantageous in experiments where spatial resolution is important, e.g. grain boundary segregation studies.

The correction procedure in bulk microanalysis is often referred to as the ZAF-correction; Z for the atomic number, A for absorption of X-rays and F for fluorescence of X-rays within the specimen. It was soon realized that if a thin electron-transparent specimen was used rather than a bulk sample, the correction procedure could be greatly simplified because, to a first approximation, the A- and F-factors are very small and only the Z-correction would be necessary.

In this work, the chemistry of grain boundaries and grain boundary phases will be investigated. As the matrix in all cases consists of aluminium, the effects of absorption of characteristic X-rays from light elements by the matrix are not significant. Absorption becomes pronounced when X-rays differ in energy by > 5-10 keV, particularly if any are light-element X-rays. According to Lynch [23] however, the effects of secondary fluorescence of Mg by Al-radiation are considerable, although Nockolds [24] on the contrary reports the fluorescence enhancement ratio to be only ~ 0.01, because of the low fluorescence yield of light elements.

All acquisitions are performed using a double-tilt specimen holder of beryllium. X-rays other than those of aluminium were not detected in the energy-dispersive-spectrum of a high purity (99.999 %) aluminium sample, indicating that fluorescence from parts of the microscope or the specimen holder can be neglected. A cold finger, cooled to liquid nitrogen temperatures, is used to reduce the hydrocarbon contamination.
2.6.2 Determination of foil thickness

A direct and accurate measure of the specimen thickness is essential for many aspects of TEM, such as correction of X-ray intensities for absorption within the specimen and for determination of actual sizes of 2D-projected features. For this purpose, convergent-beam-electron-diffraction (CBED) patterns can be used. A convergent beam of electrons is used to limit the region of specimen that contributes to the diffraction pattern. In addition to the improved spatial resolution, CBED yields information not available in selected-area-diffraction patterns. The procedure to extract the thickness from a CBED-pattern was first described by Kelly [25] and developed in detail by Allen [26]. The accuracy was reported by these authors to be ~ 2%. To get the most out of a CBED pattern, the specimen should be thicker than one extinction distance.

When exactly in a zone axis, the (000)-disc (i.e. the transmitted undiffracted beam) usually contains concentric diffuse fringes known as Kossel-Möllenstedt (K-M) fringes. The number of these fringes increases with one every time the thickness increases by one extinction distance. Thickness measurements however are not made under zone-axis conditions but under two-beam conditions with only one strongly excited (hkl)-reflection. Now the CBED discs will contain parallel instead of concentric intensity oscillations. The central bright fringe is in the exact Bragg condition. The fringe-spacing corresponds to angles \( \Delta \theta \), and from this spacing the deviation \( s_i \) for the \( i \)-th-fringe can be determined according to

\[
s_i = \frac{\lambda}{2 \theta_B d^2} \Delta \theta_i
\]

where \( \lambda \) is the wavelength of the incoming electrons, \( \theta_B \) is the Bragg angle for the diffracting (hkl)-plane (i.e. \( 2 \theta_B \) is the separation of the (000)- and (hkl)-discs) and \( d \) is the (hkl)-interplanar spacing. If the extinction distance \( \xi_g \) is known, then the foil thickness \( t \) can be determined according to

\[
\frac{s_i^2}{n_k^2} + \frac{1}{\xi_g^2 n_k^2} = \frac{1}{t^2}
\]

where \( n_k \) is an integer. These integers have to be assigned to the fringes, starting with \( n = 1 \) for the first fringe, so that the thickness \( t \) can be determined unambiguously. When this is not possible, the sample thickness may be larger than one extinction distance and \( n = 2 \) should be assigned to the first fringe.
Extinction distances for different reflections of aluminium are presented in Table 2.3. By plotting \((s_i/n_k)^2\) versus \((1/n_k)^2\), the foil thickness is given by the intercept of the resulting straight line with the \((s_i/n_k)^2\)-axis.

<table>
<thead>
<tr>
<th>Reflection</th>
<th>(\xi_{gs}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>111</td>
<td>56.3</td>
</tr>
<tr>
<td>200</td>
<td>68.5</td>
</tr>
<tr>
<td>220</td>
<td>114.4</td>
</tr>
<tr>
<td>400</td>
<td>202.4</td>
</tr>
</tbody>
</table>

2.6.3 Sample preparation

After the thermomechanical treatments are applied to the aluminium alloys, they have to be prepared for observation in the transmission electron microscope. The 3 mm-round discs are ground to a thickness of 200 \(\mu\)m and subsequently thinned using the method of electrochemical polishing. This is a rather quick method for obtaining thin, electron transparent foils with a small amount of mechanical damage. All samples were polished using a TENUPOL III device, schematically depicted in Fig 2.10a.

_Fig 2.10: TEM-sample preparation by electrochemical polishing._

(a) _Schematic setup of the TENUPOL III polishing device_

(b) _Corresponding voltage-current diagram_
Via a pump and nozzle system the electrolyte is sprayed by two jets on both sides of the specimen. A voltage is applied in order to produce a current due to anodic dissolution of the specimen and thus to create a polished surface. The voltage has to be set accurately; when it is too low, an etched surface will appear and when it is too high, a pitted surface will be the result. As shown in the diagram of Fig 2.10b, good polishing occurs on the plateau. In this work, the voltage is set to 20 V, which produces a current of ~ 0.35 A. The electrolyte used is a solution of 30 % nitric acid in methanol [28], which was cooled to a temperature of –20 °C in order to obtain a more controlled polishing process.

2.7 DETERMINATION OF THE GRAIN BOUNDARY GEOMETRY USING TEM

In order to determine the crystallographic orientation relationship between two individual grains, their orientation with respect to a specific reference should be known. The direction along which the electron beam traverses the individual crystals will be used for this purpose and its determination will be described below.

2.7.1 Determination of the beam direction

In the diffraction pattern of Fig 2.11, the beam direction is the upward direction normal to the pattern that passes through the central disc marked X. This direction can be obtained by determining its angular separation from a low-index crystallographic direction, which is defined by the crossing pairs of Kikuchi lines in the pattern. The centre P is constructed from the intersection of the grey lines drawn midway between each pair of Kikuchi lines and in this case it corresponds to the [112]-direction. The angular separation of the beam direction X from the direction [112] is obtained by making use of the camera length of the diffraction pattern, which enables conversion of the separation from millimetres into radians. The number of radians $\theta$ corresponding to one millimetre in the diffraction pattern can be calculated from the microscope’s camera length $CL$ using

$$\theta = \tan^{-1} \left( \frac{1}{CL} \right) \quad (2.7)$$
In Fig 2.11, the angular separation between points P and X can be expressed as a rotation through an angle corresponding to the distance PN about the [111]-axis from [112] in the direction of [011], followed by a rotation through an angle corresponding to the distance NX towards the direction X. Angles such as PN and NX can be determined from a typical diffraction pattern with an accuracy of about 0.1°, leading to comparable accuracy in the determination of the misorientation between two grains. However, practical difficulties sometimes arise, for instance when the low-index zone P is far removed from the central beam and cannot be projected on the photographic plate together with the central disc. In this case, zone P must be constructed from the intersection of Kikuchi lines that are extended outside the photographic plate. Another major difficulty is the presence of specimen bending, which may occur during preparation and is particularly prevalent in thin foils of soft metals. However, since it gives rise to bend contours in the image, it can easily be detected and thus be avoided if possible.

2.7.2 Determination of the crystallographic orientation relationship between two grains

In determining the orientation relationship from diffraction patterns [5], the initial data consist of a set of beam directions obtained for different crystal-orientations with respect to the electron beam. These vectors are normalized into the unit vectors \( x_r \) and \( y_r \) of grain 1 and grain 2, respectively.
The components of these vectors can then be related by a simple rotation matrix \( R \), representing a rotation \( \theta \) in a right-handed sense about an axis \( u \) with common indices \([u_1\bar{v}_1\bar{w}_1]\) in the axis systems of both individual grains, so that

\[
y_r = R \cdot x_r
\]

(2.8)

where

\[
R = \begin{pmatrix}
\cos \theta + u_1^2(1 - \cos \theta) & u_3 u_2 (1 - \cos \theta) - u_3 \sin \theta & u_2 u_3 (1 - \cos \theta) + u_2 \sin \theta \\
u_1 u_2 (1 - \cos \theta) + u_3 \sin \theta & \cos \theta + u_2^2(1 - \cos \theta) & u_1 u_3 (1 - \cos \theta) - u_1 \sin \theta \\
u_1 u_3 (1 - \cos \theta) - u_2 \sin \theta & u_2 u_3 (1 - \cos \theta) + u_1 \sin \theta & \cos \theta + u_3^2(1 - \cos \theta)
\end{pmatrix}
\]

In the case of grain boundaries, the orientation relationship thus is given by the rotation matrix \( R \). One method of determining the rotation matrix \( R \) from the experimental values of \( x_r \) and \( y_r \) is to calculate a series of values for \( u \) and \( \theta \). This method is illustrated in the stereographic projection of Fig 2.12 for a pair of beam directions \( p \) and \( q \) obtained at different sample orientations, which are specified by the unit vectors \( x_p, x_q \) (grain 1) and \( y_p, y_q \) (grain 2), respectively. For the beam direction \( p \), the rotation axis \( u \) will lie on the zone \( P \) defined by the unit vector midway between \( x_p \) and \( y_p \) and the direction normal to the zone containing \( x_p \) and \( y_p \) (i.e. the cross-product \( x_p \times y_p \)).

**Fig 2.12:**
Stereographic projection of beam directions \( p \) and \( q \).
The misorientation axis is determined by the intersection of the lines \( PP \) and \( QQ \).
In other words, \( u \) lies on the zone \( P \) given by \( P = [x_p + y_p] \times [x_p \times y_p] \). Similarly, \( u \) must also be located at the zone \( Q \) given by \( Q = [x_q + y_q] \times [x_q \times y_q] \).

Therefore, \( u \) lies at the intersection of the zones \( P \) and \( Q \)

\[
u = \frac{[P \times Q]}{|P \times Q|}
\]

(2.9)

The angle \( \theta \) is given by the angle between \( x_p \) and \( y_p \) (or between \( x_q \) and \( y_q \)) about the determined axis of misorientation \( u \)

\[
\theta = \cos^{-1} \left( \frac{[u \times x_p] \cdot [u \times y_p]}{|u \times x_p| \cdot |u \times y_p|} \right)
\]

(2.10)

The values of \( u \) and \( \theta \) obtained in this way can then be used to obtain the required rotation matrix \( R \). The final error in grain boundary misorientation is reduced significantly by considering a larger number of pairs of beam directions. It should be noted that there is generally more than one way of specifying the rotation matrix. Depending on the crystal symmetry of the grains there can be several crystallographically equivalent ways of locating each orientation map on the standard stereographic projection and this can lead to different, but equivalent assignments for the specific indices of the beam directions. This, in turn can lead to different but equivalent forms of the rotation matrix \( R \), corresponding to different but equivalent values for \( u \) and \( \theta \).

When the crystal structure is cubic, there are 24 crystallographically equivalent ways of indexing each grain, so that there are \( 24 \times 24 \) ways of expressing the orientation relationship. These occur in groups of 24, with each group having the same value of \( \theta \) and the same type of indices \( u,v,w \) for the rotation axis.

2.7.3 Determination of the grain boundary plane orientation

The last degree of freedom to be determined is the grain boundary plane orientation. As there is no rotation between the image and the diffraction pattern in the JEOL-2010F microscope, the plane can be determined by orienting the foil such that the grain boundary plane lies exactly edge-on with respect to the electron beam. From the diffraction patterns of both grains taken at this specimen orientation, the grain boundary plane can simply be found by looking for reflections of planes that are oriented parallel to the grain boundary plane.
REFERENCES