Microstructure-Property Modelling and Predictions of 7xxx Al Alloys

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The ever growing demands for high strength aluminium alloys in aerospace industry have greatly enhanced the development of alloy chemistry and thermo-mechanical treatments for optimisation of mechanical and physical property balance of 7xxx series alloys. The main objective of this work is to provide an understanding of how compositional variations and ageing treatments affect the microstructure characteristics, strength and electrical conductivity balance whilst taking account of toughness for Al-Zn-Mg-Cu 7xxx Al alloys.

This thesis has investigated the effect of compositional variations on microstructure, electrical conductivity (which is a measure of stress corrosion resistance) and yield strength balance of a wide range of Zr-containing and Cr-containing 7xxx Al alloys. Twenty-two 7xxx Al alloys within composition windows of 7010, 7x50 and 7x75 aerospace alloys have been studied and modelled. Differential scanning calorimetry (DSC), scanning electron microscopy (SEM) along with energy dispersive X-ray spectrometry (EDS), and transmission electron microscopy (TEM) have been employed to study phase transformation, grain structure, coarse intermetallic particles of these alloys. Specifically, detailed analysis of precipitation and dissolution reactions of these alloys has been investigated using DSC, and conditions for the presence of coarse intermetallic particles (S and T phase) have been analysed and interpreted in terms of physical and metallurgical principles. This has provided useful information on alloy design and thermo-mechanical processing of high strength 7xxx alloys via microstructural control.

To provide predictive tools for conductivity and yield strength, two physically based models for conductivity and yield strength have been presented in this thesis. For modelling of electrical conductivity, 9 Zr-containing and 5 Cr-containing 7xxx alloys aged at 172°C and a 7475 alloy aged at three different temperatures have been modelled. Modelling results indicate that the model can fit and predict the conductivity data of 7xxx alloys very well with an accuracy better than 1%IACS (RMSE). Specifically, the model fits best to the conductivity of 9 Zr-containing alloys with training error (RMSE) about 0.38%IACS and test error (RMSE) about 0.44%IACS, and fits the data of 6 Cr-containing alloys with training error (RMSE) about 0.56%IACS and test error about 0.61%IACS.

For strength modelling of 7xxx alloys a new model based on the Shercliff-Ashby model has been derived. The new model takes account of compositional variations and quaternary alloy systems. In general, the new model fits well to the strength data of 15 Zr-containing and 6 Cr-containing 7xxx alloys with Zn content between 5.1 to 7.5, Mg between 1.9 to 2.9, Cu between 1.2 to 2.6. The model has been applied to two ageing temperatures and nine various ageing times with the best obtainable accuracy about 21 MPa (RMSE). Modelling results indicate that the model can provide useful predictive tools for predicting the properties of 7xxx Al alloys, and in conjunction with the derived conductivity model, it is valuable from industrial point of view.


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List of Symbols and Abbreviations

List of Abbreviations

DSC differential scanning calorimetry
SEM scanning electron microscopy
TEM transmission electron microscopy
EDS energy dispersive X-ray Spectroscopy
GP zone Guinier-Preston zone
SSSa supersaturated solid solution α
EC electrical conductivity
SD standard deviation
%IACS international annealed copper standard (%) PFZ precipitate free zone
SDA solute depleted area
RMSE root mean square error

List of Symbols

α fraction transformed
β heating rate
n Avrami exponent
s kinetic exponent
$E_a, Q_A$ activation energy
$E_{eff}$ effective activation energy
$\eta_i$ impingement exponent
$A_f$ area fraction
$V_f$ volume fraction
$T_{p(\eta)}$ DSC peak temperature of $\eta'$ dissolution
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{e(n')}$</td>
<td>DSC end temperature of $\eta'$ dissolution</td>
</tr>
<tr>
<td>$HF$</td>
<td>DSC heat flow</td>
</tr>
<tr>
<td>$\Delta Q_{e(n')}$</td>
<td>reaction heat of $\eta'$ dissolution</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$q_i$</td>
<td>constant coefficient</td>
</tr>
<tr>
<td>$C_{eq}$</td>
<td>equilibrium concentration of alloying element</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>resistivity of pure Al</td>
</tr>
<tr>
<td>$R$</td>
<td>electrical resistance</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion of alloying element</td>
</tr>
<tr>
<td>$\sigma_G$</td>
<td>conductivity of the grains</td>
</tr>
<tr>
<td>$\sigma_{SDA}$</td>
<td>conductivity of solute depleted area</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>conductivity of pure Al</td>
</tr>
<tr>
<td>$\sigma_M$</td>
<td>conductivity of the matrix phase</td>
</tr>
<tr>
<td>$R_{tot}$</td>
<td>total resistance</td>
</tr>
<tr>
<td>$R_G$</td>
<td>resistance of the grains</td>
</tr>
<tr>
<td>$R_{B,L}$</td>
<td>resistance of grain boundary at L direction</td>
</tr>
<tr>
<td>$R_{B,T}$</td>
<td>resistance of grain boundary at T direction</td>
</tr>
<tr>
<td>$d_{eda}$</td>
<td>effective width of solute depleted area</td>
</tr>
<tr>
<td>$D_{Mg}$</td>
<td>diffusivity of Mg</td>
</tr>
<tr>
<td>$\rho_M$</td>
<td>resistivity of the matrix phase</td>
</tr>
<tr>
<td>$\rho_{M,P}$</td>
<td>resistivity of the pure metal</td>
</tr>
<tr>
<td>$\rho_{comp}$</td>
<td>resistivity of the matrix with particles in it</td>
</tr>
<tr>
<td>$\rho_P$</td>
<td>resistivity of particles</td>
</tr>
<tr>
<td>$\psi_p$</td>
<td>volume fraction of particles</td>
</tr>
<tr>
<td>$M_S$</td>
<td>atomic density of S phase</td>
</tr>
<tr>
<td>$M_M$</td>
<td>atomic density of matrix</td>
</tr>
<tr>
<td>$y_i$</td>
<td>fraction of the element $i$ dissolved in the matrix</td>
</tr>
<tr>
<td>$x_i$</td>
<td>concentration of alloying element $i$ in the matrix</td>
</tr>
</tbody>
</table>
$r_i$ coefficient of concentration of alloying element $i$

$\Delta H_{\text{sol}}$ enthalpy of formation per $M_a A_b B_c C_e$ unit

$\Delta H_{\text{sol}}^s$ enthalpy of formation per $\text{Al}_2\text{CuMg}$ unit

$\Delta H_{\text{sol}}^{\eta}$ enthalpy of formation per $\text{MgZn}_2$

$k(T)$ temperature dependent factor

$c_{\text{Cu}}$ equilibrium concentration of Cu in $\alpha$ phase

$c_{\text{Mg}}$ equilibrium concentration of Mg in $\alpha$ phase

$c_{\text{Zn}}$ equilibrium concentration of Mg in $\alpha$ phase

$\sigma(t)$ yield strength

$\sigma_i$ intrinsic strength of the matrix

$\Delta \sigma_{\text{ss}}$ solid solution strengthening

$\Delta \sigma_{\text{ppt}}$ precipitation strengthening

$\Delta \sigma_A$ precipitation strengthening due to particle shearing

$\Delta \sigma_B$ precipitation strengthening due to particle bypassing

$c_0$ solute concentration at equilibrium

$c_s$ start concentration of solid solution

$Q_s$ free energy of solution

$T_s$ solvus temperature

$P$ temperature-corrected time

$f_0$ equilibrium volume fraction of precipitates

$f_{\text{max}}$ maximum volume fraction of precipitates

$\tau_1$ temperature dependent factor

$P_p$ peak temperature-corrected time

$\Delta \sigma_{\text{sv}}$ initial solid solution strengthening

$\Delta \sigma_{\text{ss0}}$ final solid solution strengthening

$\sigma_q$ as-quenched strength

$\sigma_{\text{oa}}$ overaged strength
Chapter 1 Introduction

1.1 Background

The ever growing demands for high strength aluminium alloys in aerospace industry have greatly enhanced the development of alloy chemistry and thermo-mechanical treatments for optimisation of mechanical and physical property balance of 7xxx series alloys [Machler et al 1990, Morris et al 1997, Stiller et al 1998, Warner et al 1997, Liang et al 1998]. Age-hardenable Al-Zn-Mg-Cu 7xxx high strength aluminium alloys are well known to be sensitive to stress corrosion cracking (SCC), particularly when they are aged to peak strength T6 tempered condition. The stress corrosion resistance can be improved by overageing to T7 temper but a concomitant loss of about 10-15% in strength will occur [Tsai and Chuang 1996, Tsai et al 1997]. The optimised balance of properties of 7xxx alloys is largely dependent on their precipitation behaviour and microstructure characteristics.

However, although some detailed studies of the relationship between microstructure and properties of this type of alloys have been performed and tremendous efforts have been made toward improving fabrication routes and microstructural control over the years, the quantitative understanding of how compositional variations, thermal treatment conditions and processing routes affect the structure/property relations is still limited. Furthermore, the development of alloy design and quality control extensively relies on traditional empiricism. It is obvious that the pure empiricism and laboratory experiments are time-consuming and not cost-efficient, and future alloy development will no longer be driven by such experimental approaches.

To improve the efficiency of industrial fabrication and technology advancement, collaboration between research institutions and industry on modelling work of structure-property-processing relationships of aluminium alloys
Chapter 1 Introduction

is important. As a result of a research and development programme set up by Alcoa Europe Plate (the former British Aluminium Plate) in collaboration with Qinetiq (the former DERA), our research project on microstructure-property modelling and predictions of 7xxx Al alloys has begun in 1998. This thesis gathers the research work that has been completed over the past three years. Since 1998 four progress reports have been produced, and five project review meetings have been held in either Southampton or Alcoa Europe Plate.

1.2 Aims and Scope

The project is aimed at providing an understanding of how compositional variations and ageing treatments affect the strength and electrical conductivity balance whilst taking account of toughness for Zr-containing and Cr-containing Al-Zn-Mg-Cu 7xxx Al alloys. The project thus focuses on microstructure analysis and prediction of conductivity and strength in 7xxx alloys as a function of composition and heat treatment. The alloys and/or alloy data supplied by Qinetiq include 9 Zr-containing alloys initially and 6 further Zr-containing alloys, and 5 Cr-containing alloys and a commercial 7075 alloy. Besides these alloys, alloy 7475 is modelled in terms of electrical conductivity. These alloys fall in the range of typical aerospace alloys in the composition windows of 7010, 7x50 and 7x75.

To improve the thermo-mechanical treatments for optimisation of strength and toughness without significant reduction in SCC resistance, quantitative analysis of precipitation and resulting microstructure of 7xxx alloys is needed, and derivation of physically based models as well as modelling of properties of 7xxx alloys are based on the understanding of microstructural characteristics. The properties (such as strength, toughness and stress corrosion cracking resistance) of 7xxx Al alloys are greatly determined by the main phases in the alloys, i.e. GP zones, η', η, γ, T, S, MgSi and Fe-rich intermetallic phases. Thus, the balance of properties of 7xxx alloys can be optimised by microstructural modifications via alloy compositional changes and heat treatment variations. Existing literature indicates that η' / η precipitates are the main strengthening phases in 7xxx Al alloys. Coarse intermetallic particles are generally detrimental to the properties,
especially to the toughness, and in 7xxx alloys these particles are especially the Fe-rich and S (Al$_2$CuMg) intermetallic phases.

In this project, microstructure of Zr-containing and Cr-containing alloys will be studied by means of differential scanning calorimetry (DSC), scanning electron microscopy (SEM) along with energy dispersive X-ray spectrometry (EDS), and transmission electron microscopy (TEM). Detailed analysis of precipitation and dissolution reactions of these alloys will be carried out using DSC. The models for electrical conductivity and yield strength of 7xxx alloys will be derived on the basis of sound microstructure knowledge and physical principles. The models will be applied to fit and predict the conductivity and yield strength of a wide range of alloys, and also the models will be verified in terms of their accuracy and predictive capability and compared to other models.

1.3 Methodology

The research methodology chosen for this project involves a combination of modelling of properties on the basis of the microstructures of 7xxx alloys and verification of models, as well as fitting the models to data on conductivity and yield strength.

Firstly, microstructure of selected Zr-containing and Cr-containing alloys will be studied and quantified using optical microscopy, digital image analysis, DSC, SEM/EDS, and TEM. As also mentioned in section 1.2, detailed analysis of precipitation and dissolution reactions of overaged Zr-containing 7xxx alloys will be carried out using DSC. Grain structure, coarse intermetallic particles and precipitates will be studied using some of the above techniques.

Following this, conductivity models with varying complexity are to be developed by integrating amongst others Mathiesen's rule, solute depleted area, precipitation kinetics and regular solution models. The models will be used to fit and predict the conductivity data of 9 Zr-containing and 6 Cr-containing 7xxx alloys under various ageing conditions. The model for electrical conductivity of 7xxx alloys will be assessed in terms of accuracy and modelling capability and will be compared to other modelling methods.
Chapter 1 Introduction

Subsequently, the model for strength of 7xxx alloys based in part on the Shercliff-Ashby model will be established. In order to use the Shercliff-Ashby model for the modelling of yield strength of quaternary 7xxx alloys, modifications need to be made to take account of compositional variations and quaternary alloy system, as the original Shercliff-Ashby model was derived for binary alloys and is only valid for a fixed composition. With the new strength model, the modelling of the yield strengths of 21 Zr-containing and Cr-containing 7xxx alloys will be carried out, and the model or elements of the model will be verified.

1.4 Summary of the Work Conducted

Amongst the 22 7xxx alloys, 9 Zr-containing alloys and 2 Cr-containing alloys with medium Zn content and one commercial 7075 alloy are experimentally studied and their electrical conductivity and yield strength are modelled using physically based modelling approaches, whilst the rest of these alloys (including six high Zn content Zr-containing alloys and four Cr-containing alloys) are merely studied in the property modelling process. In other words, all of the 22 alloys are involved in the property modelling, either for conductivity or for strength or both, but 9 Zr-containing alloys and 3 Cr-containing alloys are investigated by a variety of analytical techniques.

A summary of the work conducted is presented in Table 1.1, indicating the alloys involved in the experiments and/or property modelling.

1.5 Thesis Overview

The work presented in this thesis highlights the microstructure analysis of Al-Zn-Mg-Cu 7xxxx Al alloys and the modelling of electrical conductivity and yield strength of these types of alloys. The thesis is structured in the following way.

In the literature review (Chapter 2), the literature associated with the basic aspects of physical metallurgy of aluminium alloys, microstructure-property relations in 7xxx alloys, as well as strength and conductivity modelling approaches is reviewed. Following a general review of physical metallurgy and processing of aluminium alloys, particular attention is given to the precipitation kinetics of 7xxx
alloys, electrical conductivity and stress corrosion resistance relations and modelling of conductivity and strengthening.

Chapter 3 deals with the materials studied, the experimental procedures and testing methods. In this thesis, 22 Zr-containing and Cr-containing 7xxx alloys are studied. The alloys for experimental studies and for property modelling are categorised, and an overview of the work conducted is presented. Optical microscopy, image analysis, DSC, SEM, TEM techniques are discussed and the experimental procedures are outlined.

Table 1.1 Summary of the work conducted

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Note: ✓ work completed at Southampton; * data available from Qinetiq; Δ data available from the literature [Hepples 1987].

In Chapter 4 the optical microscopy, SEM/EDS and TEM work is presented. The objective of this work is to provide an understanding of how compositional variations and heat treatments affect the microstructure characteristics in 7xxx alloys. Grain structures, intermetallic particles, precipitates in the selected Zr-containing and Cr-containing alloys are investigated. For the Zr-containing alloys, alloy 2 (medium Cu and medium Mg), 5 (high Cu) and 6 (high
Mg) are examined, and for the Cr-containing alloys, B2 (low Cu, Mg) and B3 (high Cu, Mg) are studied.

In chapter 5, 9 Zr-containing Al-Zn-Mg-Cu alloys and a commercial 7075 alloy with different Zn, Mg and Cu contents were investigated using differential scanning calorimetry (DSC). DSC is employed to quantitatively analyse the precipitation and dissolution of metastable and stable phases in these alloys, because it is sensitive to reactions of the main phases determining these properties, i.e. GP zones, η', η, T, S and Mg₂Si phase. DSC scans of the 9 Zr-containing alloys in various overaged conditions are presented, and the influence of compositional factors and ageing treatments on DSC heat evolution is studied. The information obtained from DSC curves is used to optimise alloy chemistry.

Chapter 6 presents conductivity models for 7xxx aluminium alloys, which are derived on the basis of physical and metallurgical principles. Four models of increasing complexity have been derived and the details of these models are discussed. The models include some of the insights obtained from the microstructural analysis presented previously. The models are subsequently used to fit and predict the conductivity data of 9 Zr-containing 7xxx alloys and 6 Cr-containing 7xxx alloys under various ageing conditions.

In Chapter 7, the yield strength of 7xxx alloys is modelled. As reviewed in chapter 2, several models or elements of models for strength in Al-based alloys have been proposed over the past decade, but models for yield strength of 7xxx Al alloys that include compositional variations have not yet been reported. In this chapter, a model applicable to yield strength of Al-Zn-Mg-Cu 7xxx alloys is described. It is based on the Shercliff-Ashby model with modifications to take account of compositional variations and quaternary alloy systems. Twenty one 7xxx alloys with various compositions and ageing conditions are modelled and analysed.

In Chapter 8, some conclusions are drawn from the investigation of microstructure of 7xxx Al alloys and the modelling of electrical conductivity and yield strength. Finally, suggestions for future work are outlined.
Chapter 1 Introduction

1.6 Contributions

This thesis investigates the effect of compositional variations on microstructure, balance between electrical conductivity (which is a measure of stress corrosion resistance) and yield strength of a wide range of 7xxx Al alloys within composition windows of 7010, 7x50 and 7x75 aerospace alloys. To provide predictive tools for conductivity and yield strength, two physically based models for conductivity and yield strength are derived and successfully used to model the conductivity and yield strength of 7xxx alloys. Specifically, major contributions to the field of aerospace materials made in this thesis are:

1. Microstructure of a number of Zr-containing and Cr-containing Al-Zn-Mg-Cu 7xxx alloys is quantitatively or qualitatively studied, particularly, phase transformations, and conditions for the presence of coarse intermetallic particles (S and T phase) are analysed and interpreted in terms of physical and metallurgical principles. This contributes to alloy design and thermo-mechanical processing of high strength 7xxx alloys via microstructural control.

2. Two detailed physics based models for electrical conductivity and yield strength of 7xxx alloys are presented in this thesis. The models provide good capability of predicting these properties, and they are new to the area of modelling of strength and electrical conductivity of 7xxx series alloys.

Several papers were written on the work presented in this thesis, and the text of some sections of the present thesis is based on these papers. This concerns especially sections 4.4, 4.5.1, 5.3.3, 6.2.3, 6.5.1, 7.2.2. The list of the papers is as follows:


Chapter 1 Introduction


d) M. J. Starink, X. Li, 2002, A Model for the Yield Strength of Al-Zn-Mg-Cu 7xxx Al Alloys”, accepted by the 8th International Conference on Aluminium Alloys, Cambridge, UK.
Chapter 2 Literature Review

2.1 Introduction

The requirement for optimum structural materials used in the aerospace industry has greatly provoked the interest of alloy manufacturers who aim to develop high strength, damage tolerant, corrosion resistant and cost-efficient alloy systems. Although structure-property relationships of high strength aluminium alloys have been extensively studied by numerous researchers over the past decades [Kirman 1971, Starke 1977, Sarkar et al 1981, Hornbogen and Starke 1993, Dorward and Beemtsen 1995], gaining the best property balance whilst taking account of production cost and fabricability still needs a sustained research effort. Recently developed methods for materials modelling enable the optimisation of structure-property-processing relationships of aluminium based materials [Sellars 1992, Ehrstrom et al 1996, Vermolen et al 1998, Starink et al 2000], despite the fact that currently alloy development and processing are still dominated by conventional empiricism. The reason why the alloy development intensively relies on experimental work other than modelling approaches is due to lack of reliable physics-based models and/or newly-arising adaptive numerical methods [Brown and Harris 1994, Christensen et al 2000] and fundamental research on modelling performance. However, it has been recognised that with the aid of materials modelling future alloy design will drastically reduce the purely empirical approaches.

In this chapter the literature associated with the basic aspects of physical metallurgy of aluminium alloys, microstructure-property relations in 7xxx alloys, as well as strength and conductivity modelling approaches is reviewed. Following a general review of physical metallurgy and processing of aluminium alloys, particular attention is given to the precipitation kinetics of 7xxx alloys, electrical
Chapter 2 Literature Review

conductivity and stress corrosion resistance relations and modelling of conductivity and strengthening.

2.2 Physical Metallurgy of Aluminium Alloys

What follows is an overview of the physical metallurgy of aluminium alloys, consisting of classification of aluminium alloys and tempers. The processing route of wrought aluminium alloys and basics of age hardening are highlighted. More detailed reviews of the physical metallurgy and processing of Al alloys are available elsewhere [Polmear 1996, Gregson 1995, Mondolfo 1976, Davis 1994].

2.2.1 Classification of Al Alloys and Tempers

Traditionally aluminium alloys have been divided into three categories: casting alloys, wrought non-heat-treatable alloys and wrought heat-treatable alloys. Casting alloys are mainly based on the Al-Si and Al-Mg alloy systems. They are generally used in small, non-loadbearing applications (e.g. components of control systems). Wrought non-heat-treatable alloys such as Al-Mn and Al-Mg based alloys do not respond to strengthening by heat treatment. Strength is developed by a combination of solid solution hardening and strain-hardening (cold-working hardening during fabrication). Wrought heat-treatable alloys such as Al-Cu, Al-Zn-Mg and Al-Li based alloys require heat treatment to develop high strength via precipitation hardening. As a general average, about 85% of aluminium alloys are used for wrought products, which are manufactured from casting ingots with the structures being greatly changed by the various working operations and thermal treatments. The wrought aluminium alloys have played a substantial role in airframe and other structural aerospace applications. These alloys, particularly 7xxx (Al-Zn-Mg based) high strength alloys will be addressed and studied in this chapter.

To classify aluminium alloys and tempers, the international alloy designation system (IADS) has been adopted (see Figure 2.1). It is noted that most Al alloys in airframe applications are of the 2xxx and 7xxx series with specific
tempers selected for property requirements. For example, fuselage structure of civil aircraft is generally constructed from 2024-T3 alloy skins having excellent damage tolerance attached to 7075-T6 alloy stringers and longerons which provide high strength.

### 2.2.2 Processing of Wrought Al Alloys

Generally, the processing of wrought aluminium alloys can be described according to the following route [Davis 1994, Polmear 1996]:

```
Ingot casting → Homogenisation → Hot rolling → Solution treatment
⇒ Quenching → Ageing treatment and/or Cold working
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Ingot-casting is adopted in the fabrication of over 90% of aluminium alloys for aerospace applications. Semi-continuous direct chill (DC) casting process is the dominant method for the manufacture of rectangular or round section billets. Low melting point major alloying additions (e.g. Zn, Mg, Cu) are added to the molten charge as pure elements, whilst high melting solutes (e.g. Ti, Cr, Zr, Mn) are added in the form of master alloys. The cast ingot grain size is controlled by small additions of Ti-B, from which the heterogeneous nuclei of TiAl₃ and TiB₂ particles are formed. The ingot is subsequently homogenised at high temperature to dissolve soluble eutectic phases (e.g. CuAl₂), reduce compositional variation and allow precipitation of small intermetallic particles (e.g. MnAl₆ and ZrAl₃) for grain structure control. The billet may be hot or cold rolled to sheet, forged close to shape or extruded to section with grain structure and texture being controlled by processing parameters and intermetallic particles. For wrought heat-treatable alloys, subsequent solution treatment, quench, natural or artificial ageing are responsible for the development of high strength [Mondolfo 1971, Polmear 1996]. During ageing homogeneous precipitation occurs via decomposition of the supersaturated solid solution, and precipitation reactions will depend on ageing temperature and vacancy concentration which, in turn, depends on solution
Chapter 2 Literature Review

treatment temperature and cooling rate. This will be discussed in more detail below.

2.2.3 Basics of Age-hardening

For an aluminium alloy to be amenable to age-hardening, it is necessary that the solid solubility of one or more of the alloying elements in the alloy decreases with decreasing temperature [Polmear 1996, Vasudevan and Doherty 1989]. Heat treatment normally involves the following stages:

A. solution treatment to dissolve the alloying elements (within the single-phase region α);
B. rapid cooling or quenching to room temperature to obtain supersaturated solid solution (SSS) of these elements in the Al-rich phase;
C. ageing at either room temperature (natural ageing) or some intermediate temperature (artificial ageing). This results in the decomposition of the SSS to produce precipitates which may form heterogeneously at preferential sites (e.g. sub-grain boundaries and dislocations) or homogeneously throughout the matrix. In the latter case, the decomposition of the SSS usually occurs by the following sequence:

$\alpha_{ss} \rightarrow$ solute atom clusters (GP zones) $\rightarrow$ intermediate precipitate $\rightarrow$ equilibrium precipitate

The complete decomposition of a supersaturated solid solution is usually a complex process which may involve several stages. Typically, GP zones and an intermediate precipitate may be formed in addition to the equilibrium phase. The GP zones are ordered, solute-rich clusters of atoms which may be only one or two atom planes in thickness. They retain the structure of the matrix and are coherent with it. The intermediate precipitate is normally much larger in size than a GP zone and is only partly coherent with the lattice planes of the matrix. It has a definite composition and crystal structure which may differ from those of the equilibrium precipitate. Formation of the final equilibrium precipitate generally involves
complete loss of coherency with the parent lattice. In heat treatable alloys, it forms only at relatively high ageing temperatures and, because it is generally coarse, little or no hardening occurs [Polmear 1996]. Maximum strengthening in commercial heat treatable alloys is caused by a critical dispersion of GP zones, or an intermediate precipitate, or both.

2.3 Precipitation, Reversion and Dissolution in Al Alloys

This section describes the general processes of precipitation, reversion and dissolution in Al alloys, especially the binary and ternary systems. The influence of vacancies and dislocations on the precipitation behaviour as well as the precipitate free zone are also discussed.

2.3.1 Precipitation in Model Alloys

As mentioned previously, some aluminium alloys display a marked response to age-hardening. By suitable addition of alloying elements and heat treatment, it is possible to increase the yield strength of pure aluminium by as much as 40 times due to precipitation hardening [Polmear 1996].

The precipitation processes may differ in accordance with the alloy systems. In solution treated and quenched Al-Si alloys, the equilibrium precipitate (the Si phase) precipitates directly from the supersaturated solid solution on ageing. As a result, Al-Si is a good model system. To study the precipitation kinetics of aluminium alloys, Starink et al. used this alloy system to study the isothermal and non-isothermal precipitation behaviour by isothermal calorimetry, DSC and TEM techniques [Starink and Zahra 1997a, 1998a, 1998b], and proposed a novel kinetic model based on the experimental data for this type of alloys. The precipitation of silicon in Al-Si alloys was also investigated by Van Rooyen et al [Van Rooyen and Mittemeijer 1989] by DSC analysis of liquid-quenched (LQ) and solid-quenched (SQ) alloys. Microstructures were characterised by XRD and TEM. It was reported that the precipitation of silicon starts earlier in LQ than in SQ alloys due to a larger driving force resulting from a larger Si supersaturation. The total exothermic heat effect for LQ alloys is caused by two processes: precipitation of Si initially
dissolved in the Al-rich phase and coarsening of Si particles already present after liquid quenching. TEM study showed that the silicon particles in the LQ alloys are much smaller than in SQ alloys, because the Si particles in the LQ alloys develop during rapid solidification or precipitate during cooling immediately after solidification.

Since the atomic volume of silicon as precipitated (diamond structure) is much larger than as dissolved in the Al-rich matrix, large stresses will develop in the Al-rich phase on ageing. Van Mourik et al have studied the kinetics of precipitation and relaxation of precipitation-induced stress in Al-Si alloys [Van Mourik et al 1987] by measuring the Al-rich phase lattice parameter, \( a_{Al} \), as a function of ageing time. Silicon precipitation from the Al-rich phase causes an overall increase of the Al-rich phase lattice parameter, but the precipitation-induced stresses and their subsequent relaxation cause a "hump" in the \( a_{Al} \) vs. time plot. The activation energy for precipitation of silicon was also calculated. For the early stages of precipitation, the activation energy for Si precipitation in solid-quenched alloys is larger (1.3eV) than that in liquid-quenched alloys (0.8eV).

The precipitation processes in the Al-Cu binary system have been studied in great detail over the last century, however, there are few commercial alloys based on this system. The Al-Cu-Mg alloy system has found many applications in the aerospace industry due to high specific strength, creep resistance and fracture toughness. Despite this, details of the precipitation mechanisms and structures of Al-Cu-Mg alloys are not as well established as those in Al-Cu alloys [Ringer et al 1996, Charai et al 2000]. Although evidence is strong for the formation of zones during natural ageing, it has not been easy to ascertain their form or size.

For the precipitation processes of Al-Cu-Mg ternary system, two different ageing paths depending on Cu:Mg ratio may arise according to the following precipitation sequences [Abis et al 1996, Alekseev et al 1993, Flower 1995]:

Supersaturated solid solution (SSS\(\alpha\)) \(\rightarrow\) GBP zones \(\rightarrow\) \(S'/S\) (\(CuMgAl_2\))

Supersaturated solid solution \(\rightarrow\) GPI/GPII zones \(\rightarrow\) \(\theta'/\theta\) (\(CuAl_2\))

The \(S'\) phase actually has the same chemical composition and structure as \(S\) and is regarded as a slightly deformed version of the \(S\) phase [Ringer et al 1996, Ringer et
Al 1998]. S phase is nucleated mostly at dislocations and has lath or rod shape [Ringer et al 1996].

Al-Zn-Mg alloys and Al-Zn-Mg-Cu alloys (7xxx series) offer the greatest potential of all aluminium alloys for age-hardening. The details of precipitation processes will be discussed in a separate section later on.

2.3.2 Influence of Vacancies and Dislocations

Considerable experimental evidence accumulated during the past twenty years indicates that a small but significant fraction of the lattice positions in most crystalline solids are not occupied by atoms but by vacancies. Diffusion of the substitutional solid-solution-forming elements as well as self-diffusion is believed to occur primarily by a vacancy exchange mechanism [Callister 1985, Van Horn 1967, Mondolfo 1976]. Therefore, vacancies are very important in the precipitation behaviour of aluminium alloys and especially the formation of GP zones in Al-based alloys. Also, dislocations formed by condensation of vacancies or by introduction of plastic strain can be very active nucleation sites for precipitation.

The importance of quenched-in vacancies in the precipitation of a second phase from a supersaturated solid solution has long been recognised, and the detailed mechanisms by which vacancies could play a structural role in precipitate formation have attracted the interest of scientific researchers [Katz and Ryum 1981, Mukhopadhyay et al 1990, Stewart and Martin 1975]. The structural role of vacancies was studied by means of microstructural observation on interstitial alloys in the work presented by Dahmen et al [Dahmen et al 1981]. The results suggested that the mechanism of vacancy-assisted precipitate formation might be much more important than previously recognised.

Ozbilen and Flower [1989] have investigated Zirconium-vacancy binding and its influence on S’-precipitation in Al-Cu-Mg alloys. It was concluded that although Zr has a very low solid solubility in Al it effectively prevents vacancy condensation into dislocation loops on quenching after solution treatment due to the very high value of solute-vacancy binding energy (measured to be 0.24±0.02eV). The reduction in dislocation loop formation strongly restricts
heterogeneous nucleation of S' precipitation in dilute Al-Cu-Mg alloys during artificial ageing, which results in coarser particle dispersions. Hence, it is worth noting that Zr should influence the precipitation behaviour of age hardenable Zr-modified Al alloys. Also, the role of vacancies on the precipitation processes in other Zr-modified Al-based alloys was stressed by Mukhopadhyay et al [Mukhopadhyay et al 1990]. The results showed that the addition of Zr to an Al-Zn-Mg alloy retards the formation of GP zones, η' and η. This is meaningful in comparing precipitation in Zr-containing 7x50 and Zr-free 7x75 alloys. Loss of excess vacancies to subgrain boundary sinks together with the modification in the distribution of free vacancies in solution is responsible for these effects.

Russell proposed a theory for excess vacancy-assisted nucleation of incoherent precipitates [Rysell 1969, Mruzik and Russell 1978]. The idea is that excess vacancies may be eliminated at the incoherent interface of the embryo thus eliminating the strain field that develops when the volume of the atoms in the embryo is larger than the matrix atoms. When eliminated in this way, the entire formation energy of vacancies is available in the nucleation process, with a consequent reduction in the nucleation barrier. The embryos are assumed to have the same physical properties as the equilibrium phase.

In a study of behaviour of excess vacancies during the nucleation of precipitates in Al-Si alloys, Ozawa and Kimura [Ozawa and Kimura 1971] showed that when a specimen is quenched from 580°C and pre-aged to give a fine dispersion of silicon precipitates, subsequent ageing at 200°C results in four distinct stages in the isothermal resistivity curve. In the first stage, dislocation loops are formed by condensation of vacancies. The loops disappear and in the second stage silicon atom clusters form. The third and fourth stages are due to precipitation of silicon atoms in a stable form. Growth and shrinkage of dislocation loops due to condensation and evaporation of vacancies during the initial stage of aging are considered important in the nucleation of silicon clusters. Also the possibilities for silicon atoms to diffuse to dislocation loops together with excess vacancies has been considered [Ozawa and Kimura 1971].
2.3.3 Precipitate-Free Zones (PFZ)

All alloys in which precipitation occurs have zones adjacent to grain boundaries that are depleted of precipitate. These zones are called Precipitate-Free Zones (PFZ). Precipitate free zones can be formed due to vacancy depletion or solute depletion or both. An investigation into an Al-4wt%Zn-3wt%Mg alloy aged at 150°C for 24 h shows that the formation of PFZs is due to two reasons: (1) there is a narrow (~50nm) region at either side of a grain boundary which is depleted of solute due to the diffusion of solute atoms into the boundary where relatively large precipitates are formed; (2) depletion of vacancies to levels below that needed to assist with nucleation of precipitates at the particular ageing temperature [Polmear 1996].

A more detailed study on the PFZs in a commercial 7075 alloy in the T6, T7 and RRA (retrogressed and reaged) tempers was carried out by Park and Ardell [1991]. The depletion of Zn and Cu atoms in the vicinity of the grain boundary was not observed in the as-quenched condition, but solute depletion developed within the PFZ during ageing. The Zn depletion was significant in the peak aged temper but did not vary further during overaging. The depletion of Cu increased as the alloy was heat-treated to the T73 condition. In the RRA condition, both the Zn and Cu concentrations were decreased markedly in the PFZ, particularly at grain boundaries. This is thought to be due to the increasing fraction of η phase at the grain boundaries during RRA as well as overaging. The decrease of Cu content in the mid-PFZs in the overaged and RRA conditions is believed to be responsible for the increased SCC resistance of the 7075 alloy in these tempers.

2.4 Structure/Property Relations in 7xxx Al Alloys

Structure-property relations in 7xxx alloys are the main focus of this literature review, as the project centres on the microstructure analysis and property modelling of 7xxx alloys. The following sections provide general knowledge in relation to the classification of 7xxx alloys, precipitation in 7xxx alloys and phase diagrams of 7xxx alloy systems. The effect of alloying elements and trace elements on the microstructure and properties is summarised. A regular solution model is
Chapter 2 Literature Review

introduced and the S phase solvus based on the regular solution model is calculated, followed by a review of recent DSC and TEM studies of 7xxx alloys.

2.4.1 Classification of Most Common 7xxx Alloys

7xxx alloys include Al-Zn-Mg and Al-Zn-Mg-Cu series. Al-Zn-Mg alloys are medium-strength alloys containing little or no copper, which have the advantage of being rapidly weldable. Al-Zn-Mg-Cu alloys have received special attention because of their high strength resulting from age-hardening. The composition ranges of the most common 7xxx alloys are listed in Table 2.1.

Table 2.1 Chemical compositions of some 7xxx aluminium alloys (wt.%)  

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si*</th>
<th>Fe*</th>
<th>Cu</th>
<th>Mn*</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti*</th>
<th>Zr</th>
<th>others</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>7010</td>
<td>0.12</td>
<td>0.15</td>
<td>1.5-2.0</td>
<td>0.10</td>
<td>2.1-2.6</td>
<td>0.05*</td>
<td>5.7-6.7</td>
<td>0.06</td>
<td>0.10-0.16</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
<tr>
<td>7040</td>
<td>0.10</td>
<td>0.13</td>
<td>1.5-2.3</td>
<td>0.04</td>
<td>1.7-2.4</td>
<td>0.04*</td>
<td>5.7-6.7</td>
<td>0.06</td>
<td>0.05-0.12</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
<tr>
<td>7449</td>
<td>0.12</td>
<td>0.15</td>
<td>1.4-2.1</td>
<td>0.20</td>
<td>1.8-2.7</td>
<td>-</td>
<td>7.5-8.7</td>
<td>-</td>
<td>0.25Ti+Zr</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
<tr>
<td>7050</td>
<td>0.12</td>
<td>0.15</td>
<td>2.0-2.6</td>
<td>0.10</td>
<td>1.9-2.6</td>
<td>0.04*</td>
<td>5.7-6.7</td>
<td>0.06</td>
<td>0.08-0.15</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
<tr>
<td>7150</td>
<td>0.12</td>
<td>0.15</td>
<td>1.9-2.5</td>
<td>0.10</td>
<td>2.0-2.7</td>
<td>0.04*</td>
<td>5.9-6.9</td>
<td>0.06</td>
<td>0.08-0.15</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
<tr>
<td>7075</td>
<td>0.40</td>
<td>0.50</td>
<td>1.2-2.0</td>
<td>0.30</td>
<td>2.1-2.9</td>
<td>0.18-0.28</td>
<td>5.1-6.1</td>
<td>0.20</td>
<td>-</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
<tr>
<td>7175</td>
<td>0.15</td>
<td>0.20</td>
<td>1.2-2.0</td>
<td>0.10</td>
<td>2.1-2.9</td>
<td>0.18-0.28</td>
<td>5.1-6.1</td>
<td>0.10</td>
<td>-</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
<tr>
<td>7475</td>
<td>0.10</td>
<td>0.12</td>
<td>1.2-1.9</td>
<td>0.06</td>
<td>1.9-2.6</td>
<td>0.18-0.25</td>
<td>5.2-6.2</td>
<td>0.06</td>
<td>-</td>
<td>0.15</td>
<td>Rem.</td>
</tr>
</tbody>
</table>

Note: * maximum contents.

2.4.2 Precipitation in 7xxx Alloys

The available literature indicates three possible precipitation sequences in 7xxx alloys, with the relative importance depending on composition [Cahn et al 1996, Deschamps et al 1999, Deschamps and Brechet 1999]. The main sequence, involving mostly Mg and Zn is thought to dominate hardening in most 7xxx alloys:

SSSα → GP zones → η' → η
A second one occurs usually at $T>200^\circ C$ and involves the $T$ ($Mg_3Zn_3Al_2$) phase:

$$SSSa \rightarrow T$$

A third one involves exclusively Cu and Mg:

$$SSSa \rightarrow S$$

where $\eta$ is a solid solution of $MgZn_2$ with $AlCuMg$ components (i.e. $Mg(Zn,Al,Mg)_2$ or $Mg(Zn_2, AlMg)$) [Wert 1981]. $S$ is $Al_2CuMg$. A structural model of the $\eta'$ phase was developed by Li et al [1999]. They found that the image simulation of this hexagonal structure revealed a good agreement between calculated and experimental high resolution lattice images using TEM.

In Al-Zn-Mg-Cu alloys, GP zones have an approximately spherical shape. The intermediate precipitate $\eta'$ and the equilibrium precipitate $\eta$ are thought to have the same hexagonal structures although the lattice parameters are different [Maloney et al 1999]. The semicoherent $\eta'$ may form from GP zones, and presents the following orientation relationship with the matrix [Deschamps et al 1997]:

$$(0001)_\eta//(111)_a \text{ and } (12\bar{1}0)_\eta//(110)_a.$$  

The incoherent $\eta$ forms at or from $\eta'$ as laths or plates. It may have one of nine orientation relationships with the matrix. The most common orientations are [Cahn et al 1996, Deschamps et al 1997, Deschamps and Brechet 1998]:

$$\begin{align*}
(10\bar{1}0)_\eta \sim (001)_a ; (0001)_\eta \sim (110)_a ; \\
\text{and } (0001)_\eta \sim (1\bar{1}1)_a ; (10\bar{1}0)_\eta \sim (110)_a.
\end{align*}$$

$\eta$ ($Mg(Zn,Al,Mg)_2$) and $T$ ($Mg_3Zn_3Al_2$) are the equilibrium phases for most commercial alloys, depending on composition [Maloney et al 1999]. The Zn:Mg ratio largely determines which of these Zn containing phases is present. For instance, Zn:Mg>2 yields $\eta$, and lower ratios yield $Mg_3Zn_3Al_2$ ($T$), hence a high Mg content causes the formation of $T$ phase. Cu contents are also important for
precipitation; Cu is present in $\eta$, and if Cu and Mg contents are high, the $Al_2CuMg$ (S) phase can precipitate. If Cu$>$Mg, CuAl$_2$ (θ) may be present [Mondolfo 1976], but in commercial 7xxx alloys, this is generally not the case.

The stability limit of GP zones has been reported to be around 120-160°C [Deschamps et al 1997]. Hence T7 7xxx alloys, which are aged at around 160-180°C, are strengthened by $\eta'$ or $\eta$ and will contain little or no GP zones. A study by Park and Ardell [1988] revealed that also in 7075 alloys at peak strength, no substantial GP zones are present, and strengthening is caused mainly by $\eta'$ precipitates. Thus, the strengthening phase for 7xxx alloys depends on the type of ageing treatments, in T6 condition it is mainly $\eta'$, whilst in T7 condition it is mainly $\eta$ or a mixture of $\eta'$ and $\eta$ [Machler et al 1991, Pitcher 1998].

### 2.4.3 Effect of Alloying Elements and Trace Elements

Extensive research work in the past decades has elucidated the effects that alloying additions and impurities have on the main properties of 7xxx alloys, and in discussing these effects it is important to note that alloying elements may be dissolved in the Al-rich phase or in intermetallic phases. Mg dissolved in the Al-rich phase renders the alloy more anodic, although dilute Al-Mg alloys retain resistance to corrosion [Polmear 1996, Vasudevan and Doherty 1989]. Cr, Si and Zn in solid solution in aluminium have only minor effects on corrosion resistance although Zn does cause a significant increase in the electrode potential. Cu reduces the corrosion resistance more than any other alloying element because of its presence in micro-constituents [Polmear 1996]. A high Mg content has a negative effect on SCC resistance, particularly Mg$>$2% is considered to be a key factor for lower SCC resistance [Polmear 1996]. Ti, which forms TiAl$_3$, may be added to refine grain size. High Mg and Cu contents, in the presence of Zr, are known to increase strength but reduce ductility and toughness.

A significant loss of toughness is observed for alloys containing 2.5% or more Cu, due to an increase in the quantity of S particles. S phase is known to degrade the toughness of 7xxx alloys [Morris et al 1997, Wagner and Shenoy 1991, Warner et al 1997].
The effect of Mg and Cu concentration on the property variations of Cu-rich 7xxx alloys in 10-50mm plate are shown in a schematic phase diagram (Figure 2.2) (adapted from Warner et al 1997). The balance of properties will determine the selection of compositions of alloys. For high strength applications, the appropriate compositions are close to the solvus of S phase, and the properties variations can vary along four main directions: two are parallel to the S phase solvus and two are normal to the S phase solvus (see Figure 2.2). For instance, increasing Mg concentration in the direction parallel to the S phase solvus causes an increase in the strength, whilst the toughness and SCC resistance at equivalent strength decrease. Increasing the Mg and Cu concentration in the direction normal to the S phase solvus causes a decrease in the toughness whilst there is little change in strength and corrosion resistance.

Fine grain size can be improved by Cr and Zr additions [Chinh et al 1998]. Commercial 7010 and 7050 Zr-containing alloys show a lower quench sensitivity than the 7075 Cr-containing alloy [Flower 1995, Suzuki et al 1983]. Mn and impurities Fe and Si cause formation of Al7Cu2Fe, MnAl6 and Mg2Si intermetallic particles. These particles will reduce the fracture toughness [Ohira 1986, Wagner and Shenoy 1991]. The main effects of alloying elements are summarised in Table 2.2.

Table 2.2 Main effects of alloying elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Main effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr, Si</td>
<td>Minor effect on corrosion resistance, refines grain size. Cr reduces recrystalization to some extend.</td>
</tr>
<tr>
<td>Ti, Zr</td>
<td>Refines grain size, Zr reduces recrystalization strongly.</td>
</tr>
<tr>
<td>Mg</td>
<td>Increases strength. Big effect on SCC, particularly for Mg&gt;2% SCC resistance decreases.</td>
</tr>
<tr>
<td>Cu</td>
<td>Increases strength but reduces toughness.</td>
</tr>
<tr>
<td>Zn</td>
<td>Main strengthening contribution, little effect on toughness and SCC resistance.</td>
</tr>
<tr>
<td>Mn, Fe and Si impurities</td>
<td>Detrimental to the fracture toughness.</td>
</tr>
</tbody>
</table>
Small addition of Ag stimulates an enhanced response of 7xxx alloys to age hardening in the temperature range of 120 to 220°C by facilitating nucleation of fine dispersions of η' [Polmear 1998]. In this case, the η' phase is generally considered to nucleate at pre-existing GP zones to which Ag segregates at an earlier stage in the ageing process. The preferred interaction of Mg and Ag may influence early clustering reactions, alter the stability of existing zones or precipitates or stimulate the nucleation of new phases. Also, addition of Ag was shown to increase resistance to SCC. An appropriate Ag content (0.5wt%) can increase tensile properties. It was reported [Caraher et al 1998] that the precipitation process was dominated by the formation of semi-coherent phases aligned parallel to {111}ₐ planes, with the similar peak hardness and overaged microstructures in several alloys containing various contents of Cu and Ag (maximum Cu content 1wt%). It was concluded that the addition of small amounts of Cu and Ag may influence the kinetics of precipitation rather than introduce new metastable precipitates when aged at 150°C.

2.4.4 Phase Diagrams

At the Al end of the Al-Zn-Mg-Cu diagram, for T>400°C five phases listed in Table 2.3 can occur [Mondolfo 1976, Strawbridge et al 1948], but of these five only the S, T and η phases appear in commercial high strength 7xxx alloys.

Figure 2.3 shows phase diagrams of Al-Zn-Mg according to Van Horn [1967]. Figure 2.4 presents a complex representation of a quaternary Al-Zn-Mg-Cu phase diagram with various compositions at 460°C and 360°C. Figure 2.5 shows the monophase fields and projection of Al-Zn-Mg-Cu alloys according to Mondolfo [1976]. Our alloys of interest lie in the oval areas indicated in these phase diagrams.

Figure 2.6 is the quaternary system Al-Cu-Mg-Zn at 460°C with 6%Zn (a) and 8%Zn (b) according to Strawbridge et al [Strawbridge et al 1948]. It is noted that our alloys of interest (with Zn concentration 5.1-6.7%, close to 6%Zn) are in the α or α + S phase fields, hence the last phase to dissolve on heating to solution treatment temperatures will be the S phase. However, the increase in Zn content
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from 6% to 8% will produce a broadening of the \((\alpha + T)\) field. Further, the increase in Zn content from 6% to 8% has caused \(\eta\) to become stable at 460°C for compositions around Al-8%wt.Zn-3%wt.Mg-2wt%Cu [Strawbridge et al 1948].

Table 2.3 Phase indications in the Al-Zn-Mg-Cu system

<table>
<thead>
<tr>
<th>Phase indic.</th>
<th>Comp. in Al-Zn-Mg (alternative indications)</th>
<th>Comp. in Al-Cu-Mg</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>(Al_2Cu)</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>(Mg_2Zn_{11})</td>
<td>(Cu_6Mg_2Al_5)</td>
<td>cubic</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>(Al_2CuMg)</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>T ((\tau))</td>
<td>(AlZnMg(Mg_3Zn_3Al_2,Al_2Mg_{11}Zn_{11},(Al,Zn)<em>{99}Mg</em>{32}))</td>
<td>(Al_6Mg_4Cu)</td>
<td>cubic</td>
</tr>
<tr>
<td>(\eta) (M, (\sigma))</td>
<td>(MgZn_2, ((Al,Zn)_2Mg))</td>
<td>(AlCuMg(Al_6Cu_4Mg_2))</td>
<td>hexagonal</td>
</tr>
</tbody>
</table>

2.4.5 Regular Solution Model

In considering the transformations in the Al-Zn-Mg-Cu 7xxx system, the key microstructural features can be characterised by two main phases: the main strengthening phase \(\eta'\) that forms in the alloys and the main coarse intermetallic phase, the S phase. For the purpose of modelling conductivity and yield strength of 7xxx alloys, it is necessary to calculate the atomic fractions of alloying elements dissolvable in the Al-rich (\(\alpha\)) phase. A regular solution model [Van Horn 1967, Starink and Gregson 1995] is selected and applied to determine the solubility of an intermetallic phase.

In this model, if the stoichiometry of a phase is assumed to be fixed, the solvus related to an intermetallic phase \(M_mA_yB_zC_c\) (\(M\) is the main constituent of the alloy, and \(A, B, C\) are the alloying elements) is given by:
\[(c_a)^a (c_b)^b (c_c)^c = c_0 \exp \left( \frac{-\Delta H_{sol}}{k_B T} \right)\]  

(2.1)

where $\Delta H_{sol}$ is the enthalpy of formation of one "molecule" of $M_{n\alpha}A_{\beta}B_{\gamma}C_{\delta}$, $k_B$ is Boltzmann’s constant and $c_0$ is a constant. If appropriate values for $\Delta H_{sol}$, $c_0$, $a$, $b$, $c$ can be derived from available solubility data, a phase diagram can be constructed. For the S phase, $\Delta H_{sol}$ in ternary alloys is available [Starink and Gregson 1996b], and by combining solvus data at 460°C [Strawbridge et al 1948] with $\Delta H_{sol}$, the S solvus as a function of the temperature can be estimated. The S phase solvus diagram was constructed by this model (see Figure 2.7).

### 2.4.6 DSC and TEM Studies on 7xxx Alloys

In a DSC thermogram of Al-Zn-Mg-Cu alloys, several main temperature regions corresponding to exothermic or endothermic effects can generally be identified according to a number of publications on DSC experiments on 7xxx alloys [Deschamps 1997, Garcia-Cordovilla 1991]. In general the following effects have been detected in DSC curves:

1. Formation of GP zones (only in freshly quenched alloys);
2. Dissolution of GP zones in the range of 50-130°C (only for underaged samples, aged at low temperatures);
3. Formation of $\eta'$ around 150°C;
4. Dissolution of $\eta'$ around 180-230°C (for overaged T7 alloys, this is the first effect to appear in a DSC curve);
5. Transformation of $\eta'$ into $\eta$;
6. Formation of T (around 200°C) [Deschamps 1997];
7. Formation of S. This effect is likely to be very small. In alloys with high Mg and/or Cu contents S phase may form after $\eta$ phase has dissolved. Hence S forms around 400-450°C.
8. Dissolution of $\eta$. The end temperature of this reaction will depend mainly on Mg and Zn contents. For most 7xxx alloys it will be around 420-470°C;
9. Dissolution of S. For high Cu alloys this reaction will continue until the solution treatment temperature 470-480°C is reached.

10. Incipient melting (sharp peaks). If Cu and Mg can not be dissolved, S can melt at about 490°C [Warmuzek 1996]. If η or T is very coarse and can not dissolve entirely during the DSC scan, these precipitates can melt around 470°C [Mondolfo 1976].

In a DSC study of effects of Zn and Cu on solid state reactions in Al-5Zn-2.3Mg (wt%) alloys with 2 wt% of either Zn or Cu addition, Garcia-Cordovilla [Garcia-Cordovilla 1991] further verified that both Zn and Cu promote nucleation of GP zones and Cu can increase the maximum temperature for zone formation, but the kinetics of phase redissolution was largely independent of Zn and Cu contents. Also it was indicated that Zn and Cu increased the quench sensitivity to some extend. Papazian [Papazian 1982] found that the precipitation and dissolution rates of metastable phases in a 7075 alloy are dominated by their reaction kinetics during a DSC scan. In contrast, the dissolution rates of stable precipitate phases (η) were dominated by thermodynamic equilibrium.

Davies et al. [1994] studied the ageing kinetics of a SiC reinforced Al-8.99Zn-2.47Mg-1.47Cu-0.13Zr (wt%) alloy using DSC, XRD (X-ray diffraction) and TEM, and revealed that the maximum rate of precipitation of the metastable η' phase was substantially lower for the MMC (metal matrix composite) as compared to the unreinforced alloy. TEM revealed the differences of these two alloys with respect to precipitate size and morphology. In this work, the possible existence of rod-like T phase was mentioned as well. Park and Ardell [Park and Ardell 1983] utilised TEM to ascertain the microstructures of commercial 7075 Al alloy in peak-aged (T651) and overaged (T7) tempers. The plate-shaped η' and equilibrium η phase were identified, but the precipitation sequences were not clearly highlighted. Delasi and Adler [1977] also investigated the peak strength (T651) and overaged (T7) 7075 Al alloys by DSC and hot stage TEM, and discussed the dissolution or formation of specific precipitates. The authors pointed out that TEM can generally be used to characterise the matrix precipitates, but the foil may not represent the bulk material and sample preparation technique may influence the results. However, using DSC in
conjunction with TEM is regarded as an effective means of phase transformation investigation of these series of alloy [Adler and DeLasi 1977, Gupta et al 1998, Sainfort et al 1997].

2.5 Kinetics of Reactions

This section deals with the kinetics of precipitation reactions, which lays the foundation for the conductivity model to be derived in section 6.2. First of all, three kinetic models, namely the JMAK model, the Austin-Rickett equation, and the Starink-Zahra model, are reviewed, followed by a discussion of activation energy and kinetic exponents for the related kinetic models.

2.5.1 Models for Kinetics of Reactions

2.5.1.1 Johnson-Mehl-Avrami Model

In the study of transformations which proceed via nucleation and growth, several mathematical descriptions of the amount transformed as a function of the time, or the transformation rate as a function of the amount transformed, have been suggested in the literature [e.g. Austin and Richett 1938, Avrami 1939a, Avrami 1939b, Johnson and Mehl 1939, Kolmogorov 1937]. In late 1930s, several researchers (Johnson and Mehl, Avrami and Kolmogorov) independently developed the well-known kinetic relation which has been extensively used to give a phenomenological description of many solid state transformation processes. It has since been referred to as the Johnson-Mehl-Avrami-Kolmogorov (JMAK), the Johnson-Mehl-Avrami (JMA) or simply the Avrami kinetic equation. The JMAK kinetic relation is based on the so-called extended volume concept which is the volume that new transformed material would occupy in the absence of impingement and overlap of adjacent transformed material. The significance of this extended volume is that it is related only to the kinetic laws of growth, which may thus be separated from the geometrical problem of impingement. The expression for the actual volume, $V_\tau$, at a reaction time of $t = \tau$ was developed by Avrami [Avrami 1939a, Avrami 1939b] in terms of the extended volume, $V_{ext}$:
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\[ V_r = 1 - \exp(-V_{ct}) \]  \hspace{1cm} (2.2)

This concept, along with an assumption of linear growth kinetics (i.e. in reactions the interface moves at a constant velocity), yielded the well-known equation for isothermal transformations:

\[ \alpha = 1 - \exp(-[K(T)t]^n) \]  \hspace{1cm} (2.3)

where \( n \) is Avrami exponent and \( K(T) \) is a thermally activated rate constant representing nucleation and growth rates which can be expressed by an Arrhenius relation:

\[ K(T) = k_0 e^{-E_a/k_BT} \]  \hspace{1cm} (2.4)

where \( E_a \) is activation energy which has contributions from both the activation energy of nucleation \( E_N \) and that of growth \( E_G \) [Cumblera and Sanchez-Bajo 1995], \( k_0 \) is a constant and \( k_B \) is the Boltzmann constant. Equation (2.3) is the so-called JMAK equation which is valid for linear growth under most circumstances and approximately valid for the early stages of diffusion-controlled growth. Equation (2.3) can also be written in the form:

\[ \ln[-\ln(1-\alpha)] = n \ln t + \ln K(T) \]  \hspace{1cm} (2.5)

Thus the Avrami exponent \( n \) can be evaluated from the slope of the plot of \( \ln[-\ln(1-\alpha)] \) against \( \ln t \).

2.5.1.2 Austin-Rickett Equation

It has been pointed out [Cahn 1956, Starink 1997] that for diffusion-controlled growth, the JMAK equation has no fundamental importance, even though it
provides a good approximation for low fractions transformed. Austin and Rickett [1938] proposed a kinetic equation which takes the following form:

\[ \alpha = 1 - \left\{ \left[ K(T) \right]^n + 1 \right\}^{-1} \]  \hspace{1cm} (2.6)

Lee and Kim [Lee and Kim 1990a, 1990b] showed that the Austin-Rickett (AR) equation fitted the transformation data for the formation (precipitation) of bainite plates in two shape-memory alloys very well. Furthermore, Lee and Kim obtained several kinetic equations by introducing an adjustable parameter termed the “impingement factor c”. They showed that c = 0 corresponds to the JMAK equation, whilst for c = 1 corresponds to the Austin-Rickett equation. Also, Starink [Starink 1997] compared the AR equation with the JMAK equation in the study of diffusion-controlled precipitation reactions and concluded that for the purpose of interpreting data of precipitation reactions, the JMAK equation is not proven to fit data of diffusion-controlled precipitation reactions whilst the AR equation is more appropriate than the JMAK equation.

2.5.1.3 Starink-Zahra Model [Starink and Zahra 1997a]

Experimental work has shown that many reactions do not conform to JMAK kinetics [Austin and Rickett 1938, Cumbra and Sanchez-Bajo 1995, Starink 1997, Starink and Zahra 1997a]. Recently (1996-98), Starink and Zahra proposed a model for the analysis of nucleation and growth reactions and showed how it can be applied to isothermal and non-isothermal transformations [Starink and Zahra 1997a, Starink and Zahra 1997b, Starink and Zahra 1998b, Zahra et al 1998]. For the isothermal case which will be adopted in the derivation of conductivity models in this thesis, the Starink-Zahra model is briefly described below.

Similar to the JMAK model the transformation is described using the so-called ‘extended volume’ concept. If all transformed volumes grow without impinging, the total transformed volume is given by \( V_{\text{ext}}(t) \). Introducing a variable \( \alpha_{\text{ext}} = V_{\text{ext}} / V_0 \), where \( V_0 \) is the volume of sample, and for the isothermal case, \( \alpha_{\text{ext}} \) can be described as:
where, similar to the JMAK model, $K(T)$ is a temperature dependent factor, $t$ is ageing time, $n$ is an reaction exponent. Next, impingement is taken into account by introducing $\lambda_i$ which is termed the impingement factor [Starink and Zahra 1997a] to obtain a general kinetic equation:

$$\frac{d\alpha}{d\alpha_{ext}} = (1 - \alpha)^{\lambda_i}$$  \hspace{1cm} (2.8)

where $\alpha$ is the fraction transformed. For $\lambda_i \neq 1$, the solution of Equation (2.8) is

$$\alpha = 1 - \left[ \frac{\alpha_{ext}}{\eta_i} + 1 \right]^{-\eta_i} \hspace{1cm} (2.9)$$

with the impingement exponent $\eta_i = 1/(\lambda_i - 1)$. Usually $\eta_i$ is between 0.1 and 3.

If there are two processes occurring whilst impingement of precipitates formed by the two processes is negligible compared with impingement between precipitates formed by the same process, i.e. if they essentially occur in independent volumes of the alloy, the sum of two processes can be obtained from a weighted average:

$$\xi = f \xi_1 + (1 - f) \xi_2 \hspace{1cm} (2.10)$$

where subscripts refer to process 1 and 2, $f$ is the volume fraction of the alloy in which process 1 occurs, $\xi$ is the amount of atoms incorporated in the growing nuclei divided by the maximum amount of atoms that can be incorporated according to the equilibrium phase diagram. For isothermal experiments, $\xi$ can be replaced by $\alpha$ in Equation (2.10).

The combination of Equations (2.7), (2.9) and (2.10) can be used to fit heat effect due to precipitation reactions for isothermal case.
Comparison of the above three models (JMAK, AR and Starink-Zahra (SZ)) reveals some common points, particularly in relation to the initial transformation stages. For instance, the kinetic mechanisms for the three models are similarly based on the 'extended volume' concept, and before impingement is taken into account, the derivation of the SZ model is nearly identical to that of JMAK model. The JMAK model, however, has only been proven to be valid for reactions with linear interface movement and not effective for diffusion-controlled precipitation reactions. The AR equation has a better fit to the experimental data for some precipitation reactions [Starink 1997], but due to the fact that the AR equation has solely a slight modification compared with the JMAK equation combined with a lack of valid kinetic experiments, it cannot be successfully considered to be a general expression for kinetic reactions. On the other hand, the SZ model incorporates nucleation, growth and impingement, takes into account the temperature-dependent solubility and distinguishes between diffusion-controlled growth and linear growth. It has been proven to have even better fits than the AR equation [Starink 1996b, Starink and Zahra 1997c, Starink and Zahra 1998b].

It is worth noting that if we look at Equation (2.8), we can find that for $\lambda_i = 1$, this equation corresponds to the JMAK equation, whilst for $\lambda_i = 2$, it corresponds to the AR equation. Hence Equation (2.8) incorporates the JMAK and the AR equation. Figure 2.8 is the graph of three models with $n=1.5$, $k=1$. Included are curves for the JMAK model, the AR model, and the SZ model ($n_i = 3$).

### 2.5.2 Other Models

About thirty years ago, Sestak and Berggren [Sestak and Berggren 1971] proposed an alternative empirical kinetic model which takes the following form:

$$f(\alpha) = \alpha^{n_i} (1 - \alpha)^{n_{ii}}$$  \hspace{1cm} (2.11)
where \( m_{SB} \) and \( n_{SB} \) are constants. In this Sestak-Berggren (SB) kinetic model, the exponential factors \( m_{SB} \) and \( n_{SB} \) have purely empirical significance. According to Cumberera et al [Cumberera and Sanchez-Bajo 1995], the behaviour of both JMAK and SB models exhibit important similarities and, moreover, it seems that the SB model is more suitable for a quantitative description of some processes, for instance, the decomposition of nickel nitrate. However, it has also been shown that the SB model cannot be successfully used as a general expression for diffusion controlled reactions. This fact, together with the lack of a physical interpretation of the constants \( m_{SB} \) and \( n_{SB} \) for solid state reactions, has determined its rather scarce use.

Speich and Fisher proposed a kinetic model (SF model) based on recrystallization kinetic experiments [Cumberera and Sanchez-Bajo 1995 and the references therein]:

\[
\frac{\alpha}{1-\alpha} = k t^{n_{SF}} \tag{2.12}
\]

where \( k \) is a constant and \( n_{SF} \) is a kinetic exponent. The above equation was based on an empirical relation between \( \alpha \) and the interfacial area \( A \) of recrystallised and unrecrystallised materials. In computer simulation work of crystallisation kinetics [Price 1987], Price demonstrated the agreement between the SF model and some experimental kinetic data. However, this author failed to realise that from mathematical conversion it can be shown that the SF equation (2.12) is equivalent to the AR equation (2.6). i.e.

\[
\frac{\alpha}{1-\alpha} = (k t)^{n_{SF}} \quad \Leftrightarrow \quad \alpha = 1 - (1 + (k t)^{n_{SF}})^{-1}
\]

Thus, the SF equation is incorporated in the Starink-Zahra model.

2.5.3 Analysis of Reactions

2.5.3.1 Analysis of Activation Energy
To determine the activation energies of reactions occurring during linear heating, several methods have been suggested, of which Kissinger analysis and Ozawa analysis are the most well-known [Starink 1996b, Starink and Zahra 1997a]. Both of these methods are so-called isoconversion methods, i.e. they are based on obtaining equal stages in the reaction (or conversion) at different heating rates. Below we will present the result of their derivations [Starink 1996b].

Generally the transformation rate during a reaction is assumed to be the product of two functions, one depending solely on the temperature, T, and the other depending solely on the fraction transformed:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]  

where \(\alpha\) is the fraction transformed and \(k(T)\) usually takes an Arrhenius expression. Through a variety of assumptions and mathematical approximations [Mittemeijer 1992, Starink 1996b], the following expression can be obtained:

\[
\ln\left(\frac{\beta}{T_f^2}\right) = -\frac{E_a}{k_BT_f} + C_1
\]  

where \(\beta\) is the heating rate, \(C_1\) is a constant which depends on the reaction stage and on the kinetic model. According to Equation (2.14), plots of \(\ln(T_f^2/\beta)\) versus \(1/T_f\) should result in straight lines, with slopes \(E_a/k_B\). This method for calculation of \(E_a\) is usually referred to as the generalised Kissinger method.

An alternative method proposed by Ozawa [Ozawa 1992] results in the following equation:

\[
\ln \beta = -1.0518 - \frac{E_a}{k_BT_f} + C_2
\]  

where \(C_2\) is an additional constant.
where $C_2$ is a constant which depends on the reaction stage and on the kinetic model. A comparison of the Ozawa and Kissinger methods shows that they both comply with the following equation:

$$\ln \frac{\beta}{T_f^{\alpha}} = -A\frac{E_a}{k_b T_f} + C_3$$

(2.16)

where $s$ is a constant, $C_3$ is a constant which depends on the reaction stage and on the kinetic model. $A$ is a constant which depends on the choice of $s$ [Ozawa 1992]. In the Kissinger method, $s=2$ and $A=1$, whilst in the Ozawa method $s=0$ and $A=1.052$. Another less known method which was proposed by Boswell [Boswell 1980] can be represented by Equation (2.16) using $s=1$ and $A=1$. It has been shown [Starink 1996b] that the Kissinger analysis is more accurate than the Ozawa and Boswell methods.

A new method for determining the activation energies from experiments performed at constant heating rate was derived by Starink [Starink 1996b]. It takes the following form:

$$\ln \frac{\beta}{T_{f,1/8}^{18}} = -A\frac{E_a}{k_b T_f} + C_4$$

(2.17)

with

$$A=1.0070-1.2\times10^{-5} E_a (E_a \text{ in kJ/mol})$$

(2.18)

where $C_4$ is a constant which depends on the reaction stage and on the kinetic model. Hence, to obtain the activation energy, the slope of a plot of $\ln(T_{f,1/8}^{18}/\beta)$ versus $1/k_b T_f$ should be calculated, whilst $A$ can be evaluated using this slope as a first approximation for $E_a$.

It was indicated [Starink 1996b] that the above expression is even more accurate than the Kissinger method. However, it should be noted that this analysis is also an isoconversion method and, hence it should be used at constant values of $\alpha$. 

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2.5.3.2 Analysis of Reaction Exponents

The reaction exponents (n, s) are characteristics of the mechanism of a reaction and contain information about nucleation rate and type of growth [Starink and Zahra 1997c]. For different kinetic models, different reaction exponents are adopted. For instance, Avrami exponent, n, applies to the JMAK model, whilst s applies to the Starink-Zahra model in linear heating case.

In the past fifteen years some authors proposed several methods to derive the Avrami exponent n [Woldt 1992, Criado and Ortega 1987, Lee and Kim 1990a, Lee and Kim 1990b]. The first two methods are based on JMAK equation, the third one is an extension of the Criado-Ortega method, but takes the impingement factor into account which does not conform to the JMAK model. However, the above methods have never been used much beyond the papers in which they were introduced.

Recently [Starink and Zahra 1997c], a new accurate method which is based on SZ model has been proposed for the determination of reaction exponent s. The reaction exponent s can be obtained from experiments performed at constant heating rate using the following equation:

\[
\frac{k_B}{\ln \dot{\varepsilon}} \frac{d}{d1/T} \cong -s(E_{\text{eff}} + 2k_B T_{av}) + 2k_B T_{av}
\]  

(2.19)

where \( T_{av} \) stands for the average temperature of the (narrow) temperature range considered, \( E_{\text{eff}} \) is effective activation energy, \( k_B \) is Boltzmann constant. By plotting the logarithm of the reaction rate versus 1/T, s can be calculated from the slope of the initial straight line. This method has been illustrated to be applicable to precipitation in Al-6%Si, GPB zone formation in Al-Cu-Mg based alloys and recrystallisation of deformed FCC metals [Starink and Zahra 1997c].
2.6 Stress Corrosion Cracking and Electrical Conductivity

Aluminium and its alloys can fail by cracking along or near grain boundaries under the combined action of a stress and corrosive environment. This phenomenon of environment-induced intergranular cracking is often called stress corrosion cracking (SCC). 7xxx series alloys are susceptible to SCC failures, and as a result, the understanding of SCC mechanisms with an aim to improve SCC resistance has to be addressed. The following sections describe the mechanisms of stress corrosion cracking, its relation to electrical conductivity and how the conductivity variations are determined.

2.6.1 Mechanisms of Stress Corrosion Cracking (SCC)

Many authors favoured anodic-dissolution based SCC mechanisms for all aluminium alloys until early 1980s, numerous studies have shown that hydrogen embrittlement (HE) generally has a role in the SCC of 7xxx series alloys and may be the dominant mechanism for 2xxx and 5xxx series alloys [Holroyd 1989, Cahn et al 1996, Staley et al 1996]. Thus two theories have evolved for SCC: one envisages it as a result of anodic dissolution of grain boundary regions under the combined influence of stress and environment; the other suggests embrittlement and loss of ductility after the ingress of atomic hydrogen into the alloy [Scamans et al 1987, Gregson 1995].

These theories were also elucidated by Polmear [Polmear 1996] who related the mechanisms of SCC to the following microstructural features. Firstly, precipitate-free zones adjacent to grain boundaries, or the grain boundaries themselves will be anodic in which strain is likely to be concentrated because they are relatively soft, and these zones are usually the initial cracking sites. Secondly, the nature of the matrix precipitates is important, especially the presence of shearable particles such as GP zones can enhance SCC. Thirdly, closely spaced dispersion of precipitate particles in grain boundaries will expedite SCC in some aged Al alloys. Moreover, hydrogen embrittlement may occur due to the rapid diffusion of hydrogen along grain boundaries.
Thus, microstructure will influence the stress corrosion behaviour. For example, the SCC susceptibility of 7xxx series alloys is strongly affected by their microstructures [Tsai and Chuang 1996a]. Tsai and Chuang considered that the increase of matrix precipitate size and the associated change from GP zones to semicoherent η' and incoherent η phase will result in a more homogeneous slip mode which can effectively reduce hydrogen transported to the grain boundaries, thus reducing hydrogen assisted SCC. On the other hand, the larger grain boundary precipitates can act as sacrificial anodes or as trapping sites for atomic hydrogen to retard intergranular SCC.

2.6.2 Stress Corrosion Cracking and Electrical Conductivity Relations

Whilst the stress corrosion resistance is relatively difficult to be quantitatively assessed, the electrical conductivity, however, can be used as a measure of the SCC resistance. In particular, SCC resistance increases with increasing conductivity in 7xxx series alloys from near peak-aged (T4) to the overaged (T73) condition [Tsai and Chuang 1996b, Ohnishi and Shiota 1986]. As electrical conductivity measurements can be made quickly and easily, this provides a convenient method for distinguishing between tempers that are prone to SCC and those that are resistant. Consequently, minimum electrical conductivity levels are identified in many corrosion resistance temper specifications as a result of its relevance to SCC [Hepples 1987, Pitcher 1998].

Electrical conductivity is used to provide assurance of satisfactory resistance to SCC for commercial 7xxx alloys, e.g. for 7010-T7651 plate, the electrical conductivity must be not less than 38.8%IACS [Pitcher 1998], and the minimum acceptable conductivity for 7475-T73 is 38%IACS [Hepples 1987].

2.6.3 Mechanisms Determining Conductivity Variations

Electrical conductivity is one of the most sensitive properties of aluminium alloys and is particularly responsive to changes in composition and thermal condition. Metallic additions to aluminium reduce its conductivity, particularly those in solid solution degrade the conductivity to a greater extent than those out of solution
Conductivity increases with increasing ageing time and temperature which is related to changes in the type and volume fraction of precipitates [Sawtell and Staley 1983, Olafsson et al 1996]. The size and distribution of the precipitates are also significant in determining conductivity variations, being responsive to changes in composition and heat treatment condition.

Barghout et al [1996] investigated the effects of second phase particles, dislocation density and grain boundaries on the conductivity of dilute Al-Fe and Al-Mg binary alloys. It was found that the second phase reduces conductivity much more significantly than dislocations and grain size. The loss of conductivity due to the presence of grain boundaries is extremely small until the grain size is reduced below 10µm where resistance increases rapidly [Barghout et al 1996].

Dorward studied the overageing kinetics of 7050 alloy and suggested that the changes in solute supersaturation (as measured by electrical resistivity) could be directly related to particle size variations, which were inferred from the DSC results [Dorward 1999]. The DSC work showed a widening of the endothermic dissolution peak and an increase of the peak temperature as ageing proceeds, which indicates the increase of precipitate size and the broadening of size distribution. The area of the dissolution peak increases with ageing time, indicating that the precipitate volume fraction increases as ageing progresses [Dorward 1999].

2.7 Modelling of Conductivity and Strength

High strength and resistance to stress corrosion cracking are important, but they are often contradictory goals for commercial 7xxx series alloys. The high strength can be obtained by high alloying element levels and by ageing to peak hardness. The resistance to stress corrosion cracking (SCC) can be achieved by reduction of alloying element levels and by overageing. Thus, it is important to achieve adequate levels of electrical conductivity, which is a measure of SCC resistance, at the required minimum strength.

Modelling work in Al alloys covers a wide range of areas incorporating the modelling of microstructural evolution, equilibrium thermodynamics and mechanical properties. For 7xxx series alloys, toughness, yield strength and
electrical conductivity are the most important properties of commercial interest. In this project, we will concentrate on the latter two properties, and in the present section we will present the literature on modelling of these properties.

2.7.1 Basic Concepts of Modelling

To derive a model, four basic steps need to be performed. Firstly, we need to identify if the model is to be a first principle model (e.g. physical/chemical model) or data based model (e.g. adaptive numeric model). Secondly, the formulation of the model (a set of equations) with adjustable parameters needs to be established. Thirdly, the algorithms or programs for identifying the free parameters should be developed. Fourthly, it is critical to validate the quality of the model or model performance, i.e. accuracy, generalisation ability (ability to predict new data), convergence, etc.

A generally applicable and rigorous method for assessing the accuracy of a model is by using the concept of training and test error, which is generally used in the field of adaptive numerical analysis. Training error is obtained from training data and test error is obtained from test data [Bishop 1995, Haykin 1999, Geman 1992]. Training data is used to identify the modelling parameters and test data is used to validate the model. With regard to the generalisation ability of a model, there are two problems that need to be resolved: underfitting and overfitting. Underfitting means that a model is not sufficiently complex to fully fit a complicated data set; whilst overfitting means that a model is too complex such that it not only fits the real signal in the training data, but also the noise. The overfitting phenomenon is mainly caused by an over-complex model (or expressions) and small training data set with noise. If the training error and the test error are close and the error is low, that means the model is a good one without underfitting or overfitting.

2.7.2 Modelling of Conductivity

Various researchers [Hatch 1983, Van Horn 1967, Olafsson et al 1996] have indicated that electrical resistivity of aluminium alloys depends on the
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concentration of atoms in solid solution, and the relationship between resistivity, temperature and composition has been given as [Olafsson et al 1996]:

$$\rho = \rho_p(T) + \rho_{rs}(c_1...c_n)$$  \hspace{1cm} (2.20)

where $\rho_p(T)$ is the temperature dependent resistivity of the pure base metal, $\rho_{rs}(c_1...c_n)$ is the contribution from the disturbances in the lattice structure from alloying elements with concentrations $c_i$.

It is noted that the effect of two or more additions on the resistivity of aluminium depends on the interaction between the elements. Overall, if the elements individually dissolve in aluminium, their effects on resistivity are additive. If a compound is formed, the solid solubility of elements may be reduced, or the compound may have a solubility of its own [Hatch 1983]. However, in the Al-Zn-Mg system, although the effect of combined presence of Mg and Zn on the resistivity of aluminium falls between the values of each alone, the contributions of Mg and Zn to resistivity are approximately additive, even when Mg and Zn are present in the ratio to form MgZn$_2$ [Hatch 1983].

In view of the modelling of conductivity, several models or elements of models have been reported, which describe the dependence of conductivity on composition and heat treatment [Bratland et al 1997, Sigli et al 1998]. For instance, a general description of thermodynamics of the Al alloy system (based on regular solution model) and the kinetics of phase precipitation (based on JMAK kinetics) was given by Bratland et al [1997].

A model which gives conductivity as a function of the microstructure was proposed by Guyot and Cottignies [1996]. This model considers conductivity increase on overageing to be due to the reduction in electron scattering resulting from the coarsening of precipitates at constant volume fraction. In the work the model was applied to one alloy (a 7075 alloy).

Dorward proposed a model that considered conductivity increase on overageing due to the reduction in the amount of dissolved atoms resulting from the coarsening of precipitates, and the model was applied to one 7xxx alloy (a 7050
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alloy) for three ageing temperatures [Dorward 1999]. The relationship between resistivity and composition is expressed as:

\[ \rho = \rho_0 + \alpha C + \beta (C_a - C) \]  

(2.21)

where \( \rho_0 \) is the resistivity of pure aluminium, \( \alpha \) is an average solute coefficient for alloying elements in solution, and \( \beta \) is a coefficient for the precipitated alloying elements having a volume fraction proportional to the difference between the total alloy content \( C_a \) and equilibrium solute concentration \( C \). The concentration of alloying elements is a time and temperature dependent factor:

\[ C - C_e = (kt)^{-1/3} \]  

(2.22)

where \( C_e \) is the solute concentration in equilibrium with particles of infinite size, and \( k \) is the rate constant:

\[ k = \frac{D(k_BT)^2}{9\gamma^2\Omega^2C_e^2} \]  

(2.23)

where \( D \) is a constant, \( k_B \) is Boltzmann’s constant, \( T \) is temperature, \( \gamma \) is the interfacial energy between the precipitate and the matrix, \( \Omega \) is the atomic volume of the particle. With these equations, the resistivity of the alloys can be modelled.

Femminella et al used neurofuzzy approaches to model the yield strength and electrical conductivity of nine 7xxx alloys. The results showed that with multiple linear regression and neurofuzzy modelling approaches the electrical conductivity can be better modelled quite well [Femminella et al 1999, Femminella et al 2000]. This of course is not a physical model, but the paper is the first publication in which a multitude of alloys is modelled.

In considering the transformation in the Al-Zn-Mg-Cu system, the key microstructural features can be characterised by two main phases: the main strengthening phase \( \eta' \) that forms in the alloys and the main coarse intermetallic phase, the S phase. For the purpose of modelling conductivity and yield strength of
7xxx alloys, it is necessary to calculate the atomic fractions of alloying elements dissolvable in the Al-rich (α) phase. The regular solution model as mentioned in section 2.4.4 has been applied to determine the solubility of an intermetallic phase. At the solution treatment temperature for the present 7xxx alloys, for the S phase, it yields [Femminella et al 1999]:

\[
(x_{Mg})(x_{Cu}) = 8.48 \times 10^5 \exp\left[\frac{-0.81eV}{k_B T}\right]
\]  

(2.24)

From this the atomic factions dissolvable in the Al-rich (α) phase \(x_{Mg,\alpha}, x_{Cu,\alpha}\) can be calculated according to the following conditions:

if

\[
(x_{Mg})(x_{Cu}) \leq 8.48 \times 10^5 \exp\left[\frac{-0.81eV}{k_B T}\right]
\]  

(2.25)

then

\[
x_{Cu,\alpha} = x_{Cu}
\]

\[
x_{Mg,\alpha} = x_{Mg}
\]  

(2.26)

wheras if

\[
(x_{Mg})(x_{Cu}) \geq 8.48 \times 10^5 \exp\left[\frac{-0.81eV}{k_B T}\right]
\]  

(2.27)

then

\[
x_{Cu,\alpha} = \frac{1}{2}(x_{Mg} - x_{Cu}) + \frac{1}{2}\sqrt{(x_{Mg} - x_{Cu})^2 + 4 \times 8.48 \times 10^5 \exp\left[\frac{-0.81eV}{k_B T}\right]}
\]

\[
x_{Mg,\alpha} = x_{Mg} - (x_{Cu} - x_{Cu,\alpha})
\]  

(2.28)

The atomic fraction of the S phase, \(x_s\) (the number of atoms present as S phase divided by the total number of atoms in the system) is given by:
2.7.3 Mechanisms of Strengthening

The relation between dislocation motion and mechanical behaviour of metals is important to the understanding of strengthening mechanisms. In general, all strengthening mechanisms rely on the simple principle: restricting or hindering dislocation motion renders a material harder and stronger. By reducing the mobility of dislocations, greater mechanical forces will be required to initiate plastic deformation. For Al-based alloys and MMCs, these mechanisms of strengthening have been studied in detail by several authors [Shercliff and Ashby 1990, Davis 1993, Gomiero et al 1992, Starink et al 1999a] and are basically ascribed to five mechanisms: 1. precipitation strengthening (involving precipitates); 2. solution strengthening (involving dissolved atoms); 3. grain and subgrain strengthening (due to hampering of dislocation movement by the presence of grain or subgrain boundaries); 4. dislocation density (due to the presence of dislocations, which have formed by prior plastic deformation); and 5. load transfer (between matrix and reinforcement in MMCs).

In commercial high-strength aluminium alloys, strengthening mechanisms can occur simultaneously or individually, and the contributions from each mechanism depend on composition, processing and fabrication, e.g. wrought, mechanically alloyed, etc. Figure 2.9 shows a schematic diagram of the relative contributions from the intrinsic strength, solid solution strength, and precipitation hardening due to shearable and non-shearable particles [Shercliff and Ashby 1990]. For heat-treatable aluminium alloys, precipitation hardening involves strengthening of grains due to precipitates. The mechanisms of strengthening for overaged 7xxx alloys, for instance, are due to the formation and presence of η’ or η precipitates [Park and Ardell 1988]. It should be mentioned that grain size reduction improves not only strength but also the toughness of many alloys.
2.7.4 Modelling of Strength

With respect to the modelling of yield strength of aluminium alloys, various models have been proposed [Shercliff and Ashby 1990, Deschamps et al 1999, Deschamps and Brechet 1999, Starink et al 1999a, 1999b]. The model derived by Shercliff and Ashby (1990) can be used to model the yield strength (or hardness) of a single binary or pseudo binary alloy as a function of ageing time and temperature. The model was applied to two 6xxx alloys and a number of binary alloys. The strength model proposed by Deschamps and Brechet [1999] allows to consider the distribution in strength of the obstacles to dislocation movement. In this work, a structural hardening model which takes account of the distribution of precipitate size was presented.

Starink et al have modelled the microstructural changes and yield strength of Al-Li-Cu-Mg alloys and MMCs using quantitative physically based models [Starink et al 1999a, 1999b]. As for the modelling of microstructural changes, the volume fractions and dimensions of strengthening precipitates of this alloy were successfully fitted using a novel transformation kinetic model. For the modelling of yield strength, a model was proposed by considering the strengthening contributions due to precipitation strengthening, solution strengthening, grain and subgrain strengthening, strengthening by dislocations and load transfer to ceramic inclusions. The model included a newly derived description of the effect of a precipitate free zone (PFZ) around the reinforcing phase incorporating strain hardening of the PFZ and it was applied to four Al-Li-Cu-Mg type alloys and composites.

Sainfort et al [1997] reported a metallurgical simulator for 7xxx alloys on the basis of data on precipitate radius and yield strength from underaged to overaged conditions, applying simulated industrial heating and cooling ramps for treatments. It was noted that using and implementing physical and metallurgical models overcomes limitations related to available data.
2.7.5 Strength-Conductivity Balance

It is recognised that the alloy composition affects the strength and electrical conductivity balance, through variation of the microstructure of the alloys. Zn:Mg ratio, Cu content and Mg content are thought to be the key compositional factors for 7xxx alloys. A high Zn:Mg ratio can offer superior SCC resistance at a given strength level, i.e. the high Zn:Mg ratio enables the alloy to retain more of its strength when it is overaged to increase its stress corrosion resistance [Speidel 1975]. The effect of Cu and Mg on the property balance is also indicated in Table 2.2 and Figure 2.2.

The relationship between strength and SCC resistance during ageing of high strength Al alloys has been studied by many researchers [Speidel and Hyatt 1972, 1975, Gregson 1995, Polmear 1996]. Figure 2.10 illustrates these variations in a schematic way: sacrifice of yield strength by overageing will result in an increase in resistance to SCC.

Sawtell and Staley [1983] have studied the effects of quenching rate and ageing temperature on yield strength and electrical conductivity of 7075 sheet (1.6mm). Specimens were solution treated and quenched in different media to achieve a wide range of cooling rates (from water quench to air-cooling). After quenching, two-step artificial ageing treatments were studied: the first ageing step was performed between 93°C and 135°C for 8-36 hours, and a second treatment of 8 hours at 171°C±1°C was applied. Figures 2.11(a-c) show how the ageing temperature, quench rate and heating rate affect the strength-conductivity balance. These figures show that especially slow heating (<20°C/min) to the ageing temperature is beneficial for the strength-conductivity balance. Figure 2.11(d) shows the effect of quench rate on the GP zone dissolution peaks in the DSC curves (QI: highest quench rate, QIII: medium quench rate, QV: lowest quench rate, Al: pure aluminium reference). It is shown that GP zone dissolution endothermic peaks decreases with decreasing the quench rate.
2.8 Summary

In this chapter the fundamental prior knowledge and current research studies with respect to the entitled project were presented. The description of physical metallurgy of aluminium alloys provides an understanding of conventional fabrication processing route of wrought Al alloys, basic aspects of age-hardening in heat treatable aluminium alloys. Alloving elements and trace elements in 7xxx alloys are critical in influencing the microstructure (e.g. precipitation and recrystalisation) and property balance (e.g. strength, SCC resistance, toughness) as well as fabricability (e.g. castability, quench sensitivity). Considerable DSC and TEM studies of 7xxx Al alloys enable us to ascertain how the microstructure changes could be affected by different composition, ageing condition and processing.

As discussed in section 2.5, kinetics of precipitation focuses on the kinetic models (either widely recognised JMAK model or newly published novel S-Z model) that are important in realising physics-based modelling approaches for 7xxx alloys. Yield strength, toughness and stress corrosion cracking (SCC) resistance, which can be reflected by electrical conductivity, are the three major properties of high-strength 7xxx Al alloys. In order to increase the SCC resistance at a desirable strength level, electrical conductivity of the alloy must reach a reasonable value that is specified in the alloy design criteria. The relationships between SCC and electrical conductivity have been well established, i.e. SCC resistance increases with increasing conductivity in 7xxx series alloys under specific heat treatment conditions.

A wide variety of research on mechanisms of strengthening indicates that impeding dislocation movement is the main mechanism for strengthening. For Al-based alloys, the mechanisms of strengthening are basically ascribed to the following mechanisms: precipitation strengthening (involving precipitates), solution strengthening (involving dissolved atoms), grain and subgrain strengthening (due to hampering of dislocation movement by the presence of grain or subgrain boundaries), dislocation density (due to the presence of dislocations, which have formed by prior plastic deformation), and load transfer (between matrix and reinforcement in MMCs). A number of strength models have been
Chapter 2 Literature Review

proposed based on the application of such mechanisms. As far as strength-conductivity balance is concerned, numerous research papers pinpoint that conductivity increases by overageing at the expense of strength.
Figure 2.1 Al alloy and temper designation (IADS) for heat-treatable aluminium alloys [Polmear 1996, Gregson 1995]. IADS stands for the international alloy designation system.
Figure 2.2 Main composition-property relations in 10-50mm 7xxx plates, adapted from Warner et al [1997].
Figure 2.3 Phase diagrams of Al-Zn-Mg alloys [Van Horn 1967]
Figure 2.4 Phase diagrams of Al-Zn-Mg-Cu with various compositions at 460°C and 360°C. The alloys of interest are in the oval area [Van Horn 1967]
Figure 2.5 (a) Monophase fields of the Al-Zn-Mg-Cu diagram. (b) projection of Al-Zn-Mg-Cu diagram, phase distribution in the solid. The alloys of interest are in the oval area [Mondolfo 1976].
Figure 2.6 Quaternary system Al-Cu-Mg-Zn at 460°C. (a) 6%Zn, (b) 8%Zn [Strawbridge et al 1948].
Figure 2.7 Solvi of S phase in Al-Zn-Mg-Cu with Zn=6wt%, temperature ranges 440-490°C.

Figure 2.8 Graph of three models with \( n=1.5, k=1\text{h}^{-1} \) and for the SZ model, \( \eta = 3 \).
Figure 2.9 A schematic diagram of the relative contributions from the intrinsic strength, solid solution strength, and precipitation hardening due to shearable and non-shearable particles [Shercliff and Ashby 1990].
Figure 2.10 Variation of strength and stress corrosion resistance during ageing of precipitation hardening Al alloys [Speidel 1975].
Chapter 2 Literature Review

Figure 2.11 Relations between yield strength, electrical conductivity, ageing treatment, quench rate and DSC heat effects of a 7075 alloy [Sawtell et al. 1983].
Chapter 3 Materials and Experimental Procedures

3.1 Introduction

In this chapter the materials studied, the experimental procedures and testing methods are presented. In the project 22 Zr-containing and Cr-containing 7xxx alloys were studied. Optical microscopy, image analysis, DSC, SEM, TEM experiments were performed on selected alloys. The alloys for experimental studies and for property modelling are categorised, and an overview of the work conducted in this thesis is presented.

3.2 Materials

The present project deals with 22 Al-Zn-Mg-Cu 7xxx alloys having different compositions. Essentially, they fall into two groups, one group consists of alloys which contain Zr as dispersoid forming element and one consisting of alloys which contain Cr as dispersoid forming element. All of the alloys fall in the range of typical aerospace alloys 7010, 7x50 and 7x75, and all but one were produced at Qinetiq, Farnborough, UK. Fifteen Zr-containing experimental alloys contain 0.02%Ti and 0.12%Zr, five Cr-containing alloys and a 7075 alloy contain 0.02%Ti and 0.18%Cr. 99.90% aluminium was used as base to ensure Fe<0.15% and Si<0.1% (all in wt%). The alloys were processed using the normal casting procedures, and after stress relaxation and homogenisation, the alloys were hot rolled to 25mm thick plate. The alloys were solution treated at 475°C for 1h and quenched and subsequently aged at 172°C and 164°C (mostly 172°C was used) for various ageing times. The details of heat treatment will be included in the
Chapter 3 Materials and Experimental Procedures

following section 3.3. The 7475 alloy was studied in terms of conductivity at three different ageing temperatures (120°C, 150°C and 180°C) for a range of ageing times, and the conductivity data of 7475 alloy was from the literature [Hepples 1987].

The chemical compositions of the alloys studied are shown in Table 3.1.

Table 3.1 Chemical compositions of the experimental alloys and some commercial 7xxx alloys (wt%)

<table>
<thead>
<tr>
<th>Alloy No</th>
<th>Zn</th>
<th>Mg</th>
<th>Cu</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-containing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.1</td>
<td>2.9</td>
<td>1.9</td>
<td>medium Zn content (Zn&lt;6.7) shaped in 25mm plate</td>
</tr>
<tr>
<td>2</td>
<td>6.1</td>
<td>2.3</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.7</td>
<td>1.9</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.1</td>
<td>2.3</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6.1</td>
<td>2.3</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.7</td>
<td>2.9</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5.1</td>
<td>1.9</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6.7</td>
<td>1.9</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6.7</td>
<td>1.9</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>7.50</td>
<td>1.96</td>
<td>1.98</td>
<td>high Zn content (Zn&gt;6.7) shaped in 25mm plate</td>
</tr>
<tr>
<td>N2</td>
<td>7.42</td>
<td>2.65</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>N3</td>
<td>6.78</td>
<td>2.41</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>N4</td>
<td>7.50</td>
<td>2.66</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>N5</td>
<td>7.11</td>
<td>2.21</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>N6</td>
<td>6.68</td>
<td>2.60</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>Cr-containing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>5.03</td>
<td>2.13</td>
<td>1.12</td>
<td>medium Zn content shaped in 25mm plate</td>
</tr>
<tr>
<td>B2</td>
<td>5.74</td>
<td>2.17</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>6.16</td>
<td>3.02</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>5.69</td>
<td>2.66</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>B5</td>
<td>6.14</td>
<td>2.54</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>Commercial</td>
<td></td>
<td></td>
<td></td>
<td>contains 0.18-0.28wt.%Cr</td>
</tr>
<tr>
<td>7075</td>
<td>5.1-6.1</td>
<td>2.1-2.9</td>
<td>1.2-2.0</td>
<td>contains 0.18-0.28wt.%Cr</td>
</tr>
<tr>
<td>7475</td>
<td>5.2-6.2</td>
<td>1.9-2.6</td>
<td>1.2-1.9</td>
<td>contains 0.18-0.25wt.%Cr</td>
</tr>
<tr>
<td>7010</td>
<td>5.7-6.7</td>
<td>2.1-2.6</td>
<td>1.5-2.0</td>
<td>contains 0.10-0.16wt.%Zr</td>
</tr>
<tr>
<td>7050</td>
<td>5.7-6.7</td>
<td>1.9-2.6</td>
<td>2.0-2.6</td>
<td>contains 0.08-0.15wt.%Zr</td>
</tr>
</tbody>
</table>
3.3 Heat Treatment

The alloys were generally solution treated at 475°C for 1 hour and cold water quenched, and subsequently aged by ramping at 20°C/hour to 172°C and holding at 172°C for selected ageing times. In order to be in accordance with this ageing conditions, our experimental samples (DSC, SEM, TEM etc.) were also solution treated and aged by ramping at 20°C/hour to 172°C and holding for various ageing times. Solution treatments at 475°C were performed at Qinetiq, ageing and testing of conductivity samples and most tensile testing were performed at Qinetiq, whilst ageing of all DSC and TEM samples as well as 7075 tensile samples were performed at Southampton.

3.4 Experimental Procedures and Testing Methods

The following sections describe the main techniques employed in this thesis, such as DSC, optical microscopy, digital image analysis, SEM/EDS and TEM. The DSC technique is particularly emphasised here.

3.4.1 Differential Scanning Calorimetry (DSC)

Of all the thermal analysis techniques differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the most versatile, with a range of applications in polymer science and pharmaceutical studies as well as in precipitation studies of metals. Both techniques are concerned with the measurement of energy changes in a substance. The word differential emphasises that measurements involve both the substance itself and a reference material [Charsley and Warrington 1992, Rechardson and Peterson 1978]. DSC is thought to be more quantitative whilst DTA is the older of the two techniques. Our research work will centre on DSC testing.

DSC has proven to be a very useful and reproducible technique for the study of phase transformations and has been widely applied to study precipitation in aluminium alloys [e.g. Archambault and Godard 2000, Gupta et al 1998, Abis et al
Besides the basic scientific interest of these studies, their underlying aim is to use calorimetry as an effective and rapid tool to investigate various characteristics of commercial alloys. For example, volume fractions of precipitates, the melting temperature of specific phases and the activation energy of reactions can in most cases be determined by the DSC technique.

3.4.1.1 Principles of DSC

There are two types of DSC: the heat flux DSC and the power compensation DSC, as shown in Fig. 3.1. For power compensation DSC, the signal is related to the differential heat provided to keep the sample and the reference to the same temperature. For heat flux DSC, the signal derives directly from the difference of temperature between the sample and the reference [Rechardson and Peterson 1978]. An example of a power compensation DSC is the Perkin-Elmer DSC7.

In our tests, a heat flux type Shimadzu DSC-50 was employed (see Fig. 3.2). For this type of DSC, samples and reference materials are simultaneously heated or cooled at a constant rate. The temperature difference between them is proportional to the difference in heat flow between the two materials. The temperature in the furnace is up to 550°C and the heat flow measuring range is from ±0.01 mW to ±100 mW. The programmable heating rate is 0.1 to 99.9°C/min.

For all the experiments a pure aluminium reference (99.9%) with a mass and shape close to that of the sample was used. Both the reference and sample were enclosed in an aluminium pan. A protective gas atmosphere of pure nitrogen was used. DSC experiments using pure aluminium as sample and reference showed that the baseline varied in an irregular manner over several days, owing to the slight differences in heat capacity between sample and reference and the imperfections of the DSC apparatus. Hence, a baseline correction experiment needs to be performed within a few days of the actual DSC experiment, and it should be performed once or twice per week. Such a baseline correction experiment consists of a single DSC run using pure Al samples.
3.4.1.2 Calibration

To achieve the full potential accuracy of the DSC technique, the DSC cell has to be calibrated [Charsley and Warrington 1992, Starink and Zahra 1997a]. To calibrate the DSC, three substances were used: Indium, Zinc and pure aluminium. The theoretical values for the melting points and the heat of fusion of In and Zn, and the heat capacity of pure Al are available from the literature. The heat flow can be calibrated by measuring the heat of fusion of In and Zn as well as the heat capacity of pure Al. The measured heat of fusion is then compared with known literature values, and the heat flow is calibrated using a calibrating factor. The temperature is calibrated by taking the deviation ΔT from the reference temperature, compared with the measured melting points of In and Zn [Starink and Zahra 1997a].

- Heat flow calibration

Three calibration experiments were carried out. The first one involved the melting of In. The maximum temperature of the DSC run $T_{\text{max}}$ should be programmed to above the melting point. From the recorded experimental curves the heat of fusion of In was measured. In order to increase the testing accuracy, the experiments at three different heat rates (i.e. 10°C/min, 4°C/min, 1°C/min) were performed and average values were calculated. The theoretical heat of fusion of In is available in the reference [Lyman 1961], hence the calibration coefficient $K_1$ with In can be calculated using the theoretical heat of fusion divided by the measured heat of fusion. The second one involved the melting of Zn. $T_{\text{max}}$ was programmed up to 440°C. The calibration coefficient $K_2$ was calibrated in the same way for the experiment with In. In the literature, three different heats of fusion of Zn are quoted: 100.94 J/g [Lyman 1961], 107.5 J/g [Horrex 1991] and 112.4 J/g [Winter 1998]. 107.5 J/g was chosen for the calculation of calibration coefficient. The third one involved the heating of pure Al. Pure Al samples were used in the first run, followed by the second run in which only one pure Al sample was used (the other side with empty crucible). The heat flow differences were measured at specific temperatures (e.g. 400K to 600K). The theoretical heat capacity of Al [Van Horn 1967] divided by the measured value corresponds to the calibration coefficient.
Chapter 3 Materials and Experimental Procedures

The calibration coefficient plotted against temperature shows a straight line (see Figure 3.3). The slope and intercept of the line are the calibration parameters which are used in the calibration software for the Shimadzu DSC-50.

- Temperature calibration

From the recorded curves for the melting of In and Zn, the melting points (or solidification points) of these two substances were measured. Compared with theoretical melting points we calculated the temperature shift ΔT.

Generally the reproducibility for the DSC experiments can be met within 1%. The DSC calibration experiment should be performed once a few months so as to assure the accuracy of the DSC cell.

3.4.1.3 Sample Preparation and DSC runs

In general, DSC sample preparation involves grinding to a thickness of about 1 mm followed by punching of discs. Alternatively, cylindrical rods may be machined and the sample discs can be cut from these rods. For our experimental studies, the latter method was used and DSC samples were machined to 5 mm in diameter and 1 mm in height with average mass of about 63 mg. DSC experiments were performed on these samples at heating rate 10°C/min. As standard procedure, each experiment contains 3 heating runs, with the latter two runs being used mainly for correction for the difference of the heat capacity of sample and reference. For instance, if the heating rate is 10°C/min, the program of the three runs is as follows: heating at 10°C/min to T_{max} (520°C), cooling at maximum rate (about -20°C/min) to room temperature, isothermal for 2h; heating at 10°C/min to T_{max}, cooling at 2°C/min to room temperature and isothermal for 1h; heating at 10°C/min to T_{max}, cooling at maximum rate to room temperature. The isothermal intervals after cooling are inserted to assure that the DSC equilibrates at room temperature.

On the issue of sample preparation technique, it is noted that Garcia-Cordovilla and Louis [1984] have investigated the influence of specimen preparation on DSC results obtained for a commercial Al-Cu based alloy AA2011
and found that in samples punched and ground after solution heat treatment, the $0'$ ($\text{Al}_2\text{Cu}$) formation effect had shifted to lower temperatures when compared to samples punched and ground prior to heat treatment. Starink et al [1996] have studied the effect of sample preparation on precipitation during DSC heating of a monolithic 8090 ($\text{Al-Cu-Mg-Li-Zr}$) alloy and an 8090 MMC. It was shown that grinding and punching of DSC samples after solution treatment alters precipitation in the 8090 monolithic alloy, whilst for the 8090 MMC grinding and punching of DSC samples after solution heat treatment has a much smaller effect. These observations could be explained by dislocation creation during grinding and punching. Thus, in DSC studies, alteration of precipitation kinetics due to dislocation creation during sample preparation should be taken into account [Starink et al 1996].

3.4.2 Optical Microscopy

Optical Microscopy was mainly used to examine the grain structures of the alloys. The apparatus used was an Olympus BH2. Three Zr-containing alloys and Two Cr-containing alloys and a commercial 7075 alloy were selected for examination. Samples were cut at about half plate thickness along the three main planes, i.e. the LT, TS and LS planes. (L = longitudinal rolling direction, T = long transverse and S = short transverse.) Specimens were mounted in bakelite and ground successively on finer carborundum papers with a final finish of 1200 grit. Subsequent polishing was performed using 6μm, 1μm and finally $\frac{1}{4}$ μm diamond paste on cloth wheels under lubricants. Carefully polished samples were used for measurement of area fraction of particles by digital image analysis and EDX compositional analysis. For grain structure examination, samples were etched in $10\text{cm}^3 \text{H}_3\text{PO}_4$ plus 90 cm$^3$ distilled water heated to 50°C for about one minute.

3.4.3 Image Analysis

Image analysis software for Windows developed by Foster Findlay Associates Limited was employed for analysis of grain structure and particles in the samples. The image analysis package is linked to the optical microscope using a high resolution digital camera for image acquisition [Boselli et al 1998]. As three
different types of particles were detected in the image, i.e. black particles, small grey particles and big grey particles, they were separated in terms of grey level threshold (100-155) and size threshold (1 μm).

3.4.4 Scanning Electron Microscopy (SEM) / Energy Dispersive X-Ray Spectroscopy (EDS)

The samples for optical microscopic examination were also used in SEM/EDS investigations. The SEM facility was a Jeol JSM-6400 Analytical Scanning Electron Microscope. In general, backscattered electron mode was used, as it is sensitive to the heavy elements, such as Cu, Zn. Different areas on the TS sections were scanned to reveal the existing particles. Chemical compositions of various particles in the samples were measured using EDS. With the available composition information, the specific particles were identified individually afterwards.

3.4.5 Transmission Electron Microscopy (TEM)

Three Zr-containing alloys (alloy 2, 5, 6) and a Cr-containing alloy (B3) were selected for TEM observation. The TEM samples were prepared by cutting a material into a thin slice (~0.3mm), and subsequently punching out a 0.3mm diameter disc and grinding to thickness around 0.15mm. The samples were electropolished using a solution of 70% methanol and 30% nitric acid, maintained at a temperature of between -20°C and -30°C [Goodhew 1984]. The TEM facility was a JEOL JEM 2000FX transmission electron microscope. An accelerating voltage of 200 kV was used.

3.4.6 Conductivity and Yield Strength Measurements

The conductivity and yield strength measurements were carried out at Qinetiq, except for the tensile tests for alloy 7075 which were conducted at Southampton University. Electrical conductivity test blocks were extracted from the heat-treated plates to provide milled surfaces at the half thickness (T/2) position. The conductivity measurements were obtained using an AutoSigma 2000 instrument,
three measurements being made for each value obtained. Care was taken to ensure that the test blocks were at laboratory temperature prior to measurement.

Transverse tensile test pieces (gauge length 31mm, diameter 5.64mm) were extracted from the heat-treated plates at the T/2 position. The tensile tests were completed in accordance with BS EN 1002-1 (1990) for proportional test pieces.
Figure 3.1 The principles of DSC. (a) Heat flux DSC and (b) Power compensation DSC. A: furnace common to sample and reference, B: separate electrical heaters for sample and reference, C: sample and reference crucibles [Rehardson 1978].
Figure 3.2 Schematic diagram of measurement cell of a Shimadzu DSC-50.
Figure 3.3 DSC calibration coefficient.
Chapter 4  Microstructure of Zr-containing and Cr-containing Alloys

4.1  Introduction

The main properties of high strength 7xxx alloys as used predominantly in aircraft wing applications are the strength, toughness and stress corrosion cracking resistance. These properties are greatly determined by the main phases in the alloys, i.e. GP zones, η', η, T, S, Mg2Si and Fe-rich intermetallic phases. Thus, the balance of properties of 7xxx alloys can be optimised by microstructural modifications via alloy compositional changes and heat treatment variations [Polmear 1996]. Coarse (larger than 1 μm) intermetallic particles are generally detrimental to the properties, especially to the toughness, and in 7xxx alloys these particles are especially the Fe-rich and S (Al2CuMg) intermetallic phases [Morris 1997]. Consequently, investigation into these intermetallic particles in 7xxx alloys with an aim to predict the properties is of key industrial interest.

The Al-Zn-Mg-Cu system is a highly complex one, with existing literature [Strawbridge et al 1948, Mondolfo 1976, Wert 1981, Villars et al 1995] indicating that at the Al end temperature between 400°C and the solidus, five intermetallic phases can occur (also see Table 2.3). Of these five, θ is essentially a binary phase (Al2Cu), S is essentially ternary (Al2CuMg), whilst η, T and Z are solid solutions with extended composition ranges containing all four elements. Of these five phases only η, T and S appear in commercial 7xxx alloys.

The objective of this chapter is to provide an understanding of how compositional variations and heat treatments affect the microstructure characteristics in 7xxx alloys. Specifically, grain structures, intermetallic particles, and precipitates in the selected Zr-containing and Cr-containing alloys will be
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

studied. For the Zr-containing alloys, alloy 2, 5, 6 are examined. Compared with typical 7010, 7050, 7x75 type compositions, alloy 5 has a high Cu content, alloy 6 has a high Mg content, whilst alloy 2 has medium Cu and Mg contents. For the Cr-containing alloys, B2 (low Cu, Mg) and B3 (high Cu, Mg) are studied.

4.2 Grain Structures

Three-dimensional grain structures of 3 Zr-containing alloys and a Cr-containing alloy are shown in Figure 4.1. Typical optical micrographs for etched samples are shown in Figure 4.2 (TS section).

Figures 4.1-4.2 reveal that all the alloys have a partially recrystallised grain structure and contain small amounts of constituent particles. The grain displays a pan-cake shape and its size is relatively small (compared with 2xxx alloys). Statistically the grain size through-thickness in the Cr-containing alloys is generally smaller than that in the Zr-containing alloys, this is in agreement with the findings of Wagner and Shenoy [1991]. The coarse particles are distributed randomly in the matrix, with the amount varying according to the alloy compositions. In the following section, these coarse particles will be quantified and discussed. The recrystallised area fractions for 3 Zr-containing alloys (2, 5, 6) and 3 Cr-containing alloys (B2, B3, 7075) were calculated from the micrographs and shown in Table 4.1.

Table 4.1 Recrystallised area fraction of Zr-containing and Cr-containing alloys(%)
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

Results in Table 4.1 show that the recrystallised area fraction of three Zr-containing alloys is around 24 to 39%. Alloy 6 has the highest recrystallised area fraction at about 39%, whilst that of alloy 5 is lower at about 24%. For the 2 experimental Cr-containing alloys, the recrystallised area fraction is much higher than that of Zr-containing alloys (above 50%), but the commercial 7075 alloy has a low recrystallisation (19%), which is the lowest of all the 7xxx alloys. It is worth noting that recrystallisation reduces toughness and increases quench sensitivity of the alloys, it should therefore be limited to a low level.

4.3 Intermetallic Particles

A digital image analysis package was used to study the intermetallic particles in the alloys. Three cross sections (LT, TS and LS) of samples of Zr-containing alloys 2, 5 and 6, as well as Cr-containing alloys B2, B3 were examined. Figure 4.3 presents an image of alloy 2-TS, showing three types of particles, i.e. black particle (colour threshold 0-99), big grey particle (colour threshold 100-155, size threshold >1μm), and small grey particle (size<1μm).

The area fraction of each type of particle was measured and results are summarised in Table 4.2. The total area fraction of particles for 3 Zr-containing alloys and 2 Cr-containing alloys is plotted in Figure 4.4. The results indicate that for Zr-containing alloys, the high Cu alloy has the highest percentage of coarse particles, which indicates that Cu plays an important role in the formation of coarse particles. For Cr-containing alloys, B3 with high alloying element contents has a higher volume fraction of coarse particles than low alloying element content B2. Overall, the amount of coarse particles in these Zr-containing alloys appears to be more than that in these Cr-containing alloys.

In order to identify the coarse particles in Zr-containing and Cr-containing alloys, alloy 5 and alloy 6, B2, B3 were studied using SEM/EDS. Figures 4.5-4.8 show the SEM micrographs of alloys 5, 6, and B2, B3. Table 4.3 presents some examples of the chemical compositions of the particles obtained from EDS, with identification of the phases. Note that in all cases the Al rich matrix contributes to the compositional analysis.
**Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys**

Table 4.2 Volume fractions of particles in Cr-containing and Zr-containing alloys (%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Volume Fractions (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr-containing</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>0.46</td>
<td>0.58</td>
</tr>
<tr>
<td>B3</td>
<td>1.35</td>
<td>1.15</td>
</tr>
<tr>
<td>Zr-containing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.29</td>
<td>1.34</td>
</tr>
<tr>
<td>5</td>
<td>3.51</td>
<td>1.61</td>
</tr>
<tr>
<td>6</td>
<td>1.15</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Table 4.3 EDS compositional analysis of typical particles in Zr-containing and Cr-containing alloys (at.%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Particle</th>
<th>Al</th>
<th>Cu</th>
<th>Mg</th>
<th>Zn</th>
<th>Fe</th>
<th>Ti</th>
<th>Si</th>
<th>Zr</th>
<th>Cr</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-containing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>type 1</td>
<td>70.83</td>
<td>14.39</td>
<td>13.41</td>
<td>1.31</td>
<td>0.04</td>
<td>--</td>
<td>0.00</td>
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<td>3.50</td>
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</table>
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

It is noticed that, for the alloy 5, the detected particles are mostly S phase (diameter ~3μm, evenly distributed particles) and Al7Cu2Fe (typically ~15μm, clustered in bands). For the alloy 6, the detected particles are mostly S phase and a complex phase containing Cu, Mg, Zn and probably Al, but due to the contribution of the matrix to the EDS signal the latter could not be unambiguously determined. Based on a comparison of the measured composition with composition ranges proposed for Cu, Mg, Zn containing phases [Mondolfo 1976, Strawbridge 1948], this phase was identified as T phase. The T phase is based on the composition Mg3Zn3Al12. There are further very few Al7Cu2Fe and Si containing particles in the alloy 6. The Si containing particles remain, as yet, unidentified.

It is also observed that the detected particles in B2 are mostly irregularly shaped Al7Cu2Fe with various sizes (largest up to 20μm in length). There is hardly any S phase across the section, although throughout the scan a type of small round particle was observed and identified as S phase. For B3, the detected particles are mostly S phase and Al7Cu2Fe. There also exists a further kind of complex particle, as shown in Table 4.3 (type 5 and type 6), part of it being Ti, Fe containing phase and part of it being Fe, Cu containing phase (with more Fe than Cu, so it could not be Al7Cu2Fe phase). This coarse particle cannot be clearly identified in terms of the available phase diagrams, but seems to be caused by the impurities. The main particles in 7075 are Al7Cu2Fe and no S phase was detected. Further, a few Cr containing particles were detected in 7075, and according to the work by Davis [Davis 1994] this could be (Fe,Cr)sSiAl12 intermetallic constituent formed during solidification or Cr2Mg3Al18 dispersoids formed during homogenisation. As the Mg content is very low, it is thus unlikely to be Cr2Mg3Al18 dispersoid.

Figure 4.9 shows a DSC curve with three runs of Alloy 5 aged at 172°C for 16h. Comparison with other work [Garcia-Cordovilla 1991, Deschamps et al 1997] allows identification of the heat effects: peak A corresponds to the dissolution of η', B the formation of η and C the dissolution of η. Effect D and E are ascribed to the formation of S phase and the dissolution of S phase, respectively. As will be discussed below, this identification is consistent with solvus data of S phase. Effect G is due to the melting of undissolved S phase [Morris et al 1997]. Effect F corresponds to the melting of T phase and is only observed in the third DSC run. This indicates that after very slow cooling (2°C/min), there was not sufficient time
for the coarse T phase to be completely dissolved, and hence a melting of T phase occurred at 480°C. The difference between the three DSC runs was caused by the heating cycles of DSC, for instance, in the second run the first exothermic peak corresponds to the $\eta'$ precipitation and there is a GP zone dissolution effect prior to the $\eta'$ precipitation effect. Detailed identification of DSC heat effects and DSC observations of 9 Zr-containing alloys will be presented in Chapter 5. Figure 4.10 presents DSC curves of three alloys (2, 5, 6) aged at 172°C for 16h (heating rate 10°C/min). It is noticed that the high Cu alloy 5 has the strongest S melting peak, followed by the high Mg alloy 6 and medium Cu and Mg alloy 2.

In order to further investigate the presence of T phase in the high Mg alloy 6 and confirm our interpretations, samples were solution treated for 1 h at 437, 452, 467 and 485°C. In samples solution treated at 437 and 467°C two melting peaks, corresponding to T melting at 480°C and S melting at 490°C, were observed, see Figure 4.11. These DSC curves show that the T phase melting peak decreases with increasing solution treatment temperature. Additional SEM/EDS studies on alloy 6 solution treated at 485°C revealed that the T phase had totally disappeared. These results indicate that the T phase, which is thought to form during casting, is not stable at the solution treatment temperatures employed and that with increasing solution treatment temperature the T phase either dissolves, to be replaced by S phase, or transforms directly to S phase.

To summarise the particles of Cr-containing 7xxx alloys, it is clear that Al$_7$Cu$_2$Fe is the major intermetallic particle whilst S phase can be eliminated by adjusting Cu, Mg contents and solution treatment temperature according to S phase solvus.

### 4.4 Precipitates

It is well recognised that the precipitation sequence in 7xxx alloys can take three main forms depending on composition and ageing (see section 2.4), and the maximum strength is achieved when $\eta'/\eta$ precipitation is involved [Sawtell and Staley 1983, Park and Ardell 1988]. In this work, DSC was used to study the formation and dissolution of precipitate phases in the alloys, whilst TEM was employed to reveal the fine microstructure of the alloys. TEM experiments were
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

performed on the selected alloys 5, 6 and B3 at different ageing conditions. Typical TEM micrographs are shown in Figures 4.12-4.15.

TEM investigation revealed the fine microstructure features of the alloys: precipitates in the matrix, grain (or subgrain) boundaries and PFZs. Figure 4.12 shows the fine precipitates in the matrix and subgrain boundaries. Figure 4.13 shows bigger precipitates decorating on the grain (or subgrain) boundaries, which correspond to the equilibrium η phase [Srivatsan et al 1997]. PFZs adjacent to the boundaries are also observed. The coarse η precipitates are about 50 nm in diameter. There are two reasons why the precipitates on the grain boundary are much bigger than that of the matrix. Firstly the rapid diffusion of solute atoms into the boundary as a result of the formation of PFZs causes the relatively large precipitates. Secondly in the PFZs the depletion of vacancies to levels below that needed for nucleation sites results in formation of coarse precipitates [Polmear 1996]. Obviously (see Figure 4.13 a and b), the precipitates for long ageing time (16 hours) are much coarser than the ones for short ageing time (4 hours).

A typical TEM micrograph of the Cr-containing alloy (B3) is shown in Figure 4.14, with intermetallic particles being present in the matrix. The size of the precipitates in the matrix is about 10-30 nm in diameter. Based on the previous SEM/EDS observations, the spherical shaped particles are possibly S phase (see Figure 4.14a), whilst the bar-shaped particles are likely to be Al<sub>2</sub>Cu<sub>2</sub>Fe intermetallics (see for instance, Wagner and Shenoy 1991). It is also observed that there are some solute depleted areas in the vicinity of the particles. The formation of these areas is similar to the formation of PFZs adjacent to grain boundary. Initially, during ageing a few precipitates (possibly η) form around the edge of the particle and due to the diffusion of solutes to the precipitates, the precipitates grow and the solute depleted areas adjacent to the particle are formed. The present observations of bar-shaped Al<sub>2</sub>Cu<sub>2</sub>Fe intermetallics with solute depleted areas are in good agreement with the observations on Cr-containing 7xxx alloys by other researchers [Wagner and Shenoy 1991].

Figures 4.15-4.16 illustrate the diffraction pattern of an overaged sample of the Al-6.7Zn-2.9Mg-1.9Cu (alloy 6) and the illustrative sketch of the diffraction pattern, respectively. The bright spots on the diffraction pattern are due to the reflection of Al matrix, whilst the fainter spots and streaks appeared in a cross-like
pattern remain controversial according to available literature. For instance, Park and Ardell [1983], Deschamps and Brechet [1998] regarded this pattern as the reflection of \( \eta \), whereas Stiller et al [1998] attributed this to the reflection of \( \eta' \) phase. Based on the ageing conditions of the alloys studied (T73) and the corresponding DSC curves (see next chapter), this symbol is suggested to be the reflection of the \( \eta \) phase.

4.5 Discussion

4.5.1 Conditions for the Presence of \( S \) and \( T \) Phase

In interpreting the results, we will make use of a temperature dependent solvus diagram for \( S \) phase estimated from the regular solution model (see section 2.4.5) as well as published phase diagrams at 460°C (see Figures 4.17-4.18). As no DSC experiments were performed on the Cr-containing alloys, and SEM/EDS results for Cr-containing alloys indicated the same mechanism for the formation of coarse intermetallics as the Zr-containing alloys, we will only discuss conditions for the presence of \( S \) and \( T \) phase in the selected Zr-containing alloys below.

The \( S \) phase solvus (Figure 4.17) indicates that at a solution treatment temperature of 475°C, alloys 5 and 6 are in the \((\alpha+S)\) field, thus \( S \) phase can not be dissolved in these alloys at this temperature. Alloy 2 is practically on the \( S \) phase solvus, and given sufficient solution treatment time, \( S \) phase would be expected to dissolve. However, some compositional segregation originating from the solidification process can cause \( S \) phase to remain present even after long solution treatment time. The observed \( S \) phase melting peaks in Figure 4.10 are in line with this interpretation. Figure 4.17 indicates that dissolution of \( S \) phase is possible for alloy 6 through increasing the solution temperature to just below 490°C, whilst complete dissolution of \( S \) phase is impossible for alloy 5. For the high Mg alloy 6, both \( S \) melting at 490°C and \( T \) melting at 480°C were present. The latter may seem surprising as, according to the phase diagram of Al-Zn-Mg-Cu alloys with 6wt%Zn at 460°C (Figure 4.18, based on data from Strawbridge et al. [1948]), \( T \) phase only appears for alloys with Mg content higher than 3.2wt%, i.e. alloy 6, which contains 2.9wt%Zn, is within the \( \alpha+S \) phase field. However, the \( \alpha+S+T \)
phase field in the phase diagram at compositions around alloy 6 expands substantially with increasing Zn content, such that for a Zn content of 8wt% at 460°C, T phase is stable for Mg contents as low as 2.7wt% [Strawbridge et al 1948]. This suggests that alloy 6, at the solution treatment temperatures used, may be in or very close to the α+S+T phase field. A small amount of Mg segregation, which originates from the solidification processing and which is not entirely removed during the thermomechanical and thermal processing, can thus cause the presence of T phase in alloy 6. This finding will have consequences for solution treatment practice of 7xxx alloys, i.e. the 7050 and 7010 alloys which have Mg contents lower than 2.6wt%, are not expected to contain T phase and, provided they are well homogenised, they can be solution treated up to the incipient melting temperature of S phase (490°C). However, for alloys with Mg contents at the high end of the 7075 composition range (2.9wt%), some T phase can be present and they should be solution treated below the melting point of T phase (480°C).

In general, the DSC data on S phase and T phase melting are in good agreement with the SEM/EDS observations. It is also noted that the identification of effect E in the DSC curve of the high Cu alloy 5 (Figure 4.9) as due to the dissolution of S phase is consistent with the S phase solvus in Figure 4.17, as the latter indicates that on heating, substantial S phase dissolution should occur from about 440°C. On further heating, the original solution treatment temperature will be reached and further dissolution of S phase would involve the coarse S phase particles left undissolved after the solution treatment (475°C). As dissolution of these coarse particles will be slow, the S phase dissolution effect during DSC heating would be expected to decrease substantially at this temperature. This explains why the S phase dissolution effect is situated between about 440 and 475°C, and lends further support to our earlier interpretation of effect E.

4.5.2 Microstructure Variations in Zr-containing Alloys and Cr-containing Alloys

The effect of addition of Zr or Cr to 7xxx series alloys has been well evaluated [Conserva and Fiorini 1973, Wagner and Shenoy 1991, Engler et al 1996]. Generally, the addition of Zr or Cr improves grain structure and reduces
recrystallisation in 7xxx alloys through precipitation of finely distributed dispersoids, i.e. ZrAl₃ for Zr-containing alloys and Cr₂Mg₅Al₁₈ for Cr-containing alloys (it is also called Cr-rich E phase) [Davis 1994, Conserva and Fiorini 1973]. As shown in the Table 4.1, the recrystallised area fraction of Zr-containing alloys is less than that of Cr-containing alloys, being attributable to Zr reducing recrystallisation more effectively than Cr. As recrystallisation has direct influence on yield strength and toughness of 7xxx alloys, by decreasing yield strength and toughness with increasing recrystallisation fraction [Dorward and Beemtsen 1995], it is, hence, a major concern for selection of materials for aerospace applications.

SEM/EDS results showed that Cr-containing alloys contained the same type of main intermetallics as Zr-containing alloys (see Table 4.2, Figures 4.5-4.8), and the difference in the amount of intermetallics particles was caused by overall composition variations. Similarly, from the TEM observations it was apparent that either Zr or Cr had no noticeable effect on the precipitates in the alloys, although theories indicate that Zr affects precipitation kinetics by retarding GP zones and η' formation and slowing down η precipitation [Mukhopadhyay et al 1990]. This effect might lead to smaller size of η precipitates in Zr-containing alloys than those in Cr-containing alloys, which was discerned by Conserva and Fiorini [1973].

One of the advantages that the Zr-containing alloys have over the Cr-containing alloys is their reduced quench sensitivity (the term quench sensitivity indicates the reduction in ageing hardening capability induced by low quenching rates) [Polmear 1996, Gregson 1995, Suzuki et al 1983]. The reason for the quench sensitivity improvement by Zr is due to the fact that Zr-containing dispersoids are less likely to be the nucleation site for η formation during cooling as compared to Cr-containing dispersoids. This is because Al₅Zr dispersoids are generally coherent with the matrix. It is generally believed that incoherent dispersoids are more effective as nucleation sites for η formation [Suzuki et al 1983].

The influence of Zr and Cr on the strength and toughness of 7xxx alloys largely depends on particular ageing conditions. For instance, some authors found that Zr-containing alloys in the T8 condition exhibited higher strength and toughness than Cr-containing alloys, whilst in the T73 condition, Cr-containing alloys were tougher than Zr-containing alloys [Chen and Knott 1981, Wagner and Shenoy 1991]. As all alloys were in overaged conditions (T7), in combination with
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

the low volume fraction of coarse intermetallic particles for the Cr-containing alloys, it is expected that the Cr-containing alloys could have a better fracture toughness than the Zr-containing alloys.

4.6 Conclusions

Optical microscopy, digital image analysis, SEM/EDS, TEM and DSC were employed to study grain structure, coarse intermetallic particles, precipitates in Zr-containing and Cr-containing alloys. The main conclusions can be drawn as follows:

1. For all the alloys investigated, optical microscopy revealed a partially recrystallised grain structure with about 20–40% recrystallised area fraction for the Zr-containing alloys and over 50% for the Cr-containing experimental alloys, and about 20% for the commercial 7075 alloy. Unrecrystallised grains show a pan-cake shape.

2. The recrystallised area fraction of Zr-containing alloys is less than that of Cr-containing alloys, being attributable to Zr reducing recrystallisation more effectively than Cr. As recrystallisation has direct influence on yield strength and toughness of 7xxx alloys, it remains a major concern for selection of materials for aerospace applications.

3. With regard to coarse particles in the Zr-containing alloys, SEM/EDS indicated that in the high Mg alloy the main coarse particles are S (Al₂CuMg) and T (Mg₂Zn₃Al₂), whilst in the high Cu alloy they are S and Al₇Cu₂Fe. The high Cu alloy has the highest volume fraction of coarse particles. These results are consistent with the DSC observations. SEM/EDS experiments on the Cr-containing alloys indicated that the conditions for the presence of coarse particles are of little difference between Cr-containing and Zr-containing alloys, and the detected particles are mainly S phase, Al₇Cu₂Fe, as well as Cr, Fe-rich intermetallic particles.
4. All observations on the presence and melting of coarse intermetallic phases can be interpreted well on the basis of phase diagrams and the temperature dependent S phase solvus based on the regular solution models. It is shown that some compositions in the composition windows of 7050 and 7x75 type alloys will give rise to the detrimental S phase which cannot be dissolved during solution treatment. Results indicate that T phase is present only if Mg content approaches the high Mg end of the composition range for the 7075 alloy (2.9wt% Mg).
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

Alloy 2, low magnification

(a)

Alloy 2, high magnification

(b)
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

Alloy 5, low magnification

Alloy 5, high magnification
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

Alloy 6, low magnification (e)

Alloy 6, high magnification (f)
Fig. 4.1(a)-(h) Three-dimensional grain structures of alloys 2, 5, 6 and B3 at high magnification and low magnification.
Chapter 4 Microstructure of Zr-containing and Cr-containing alloys

Alloy 2-LS (a)

Alloy 2-TS (b)
Chapter 4 Microstructure of Zr-containing and Cr-containing alloys

Alloy 6-TS

Alloy 6-TS
Figure 4.2 (a)-(l) Optical micrographs of etched samples of alloys 2, 5, 6, B3 and 7075
Figure 4.3 The image of an unetched sample (alloy 2, medium Cu and Mg, TS direction), showing the coarse particles in the matrix. A: black particle, B: big grey particle, C: small grey particle.
Figure 4.4 Volume fraction of coarse particles in three Zr-containing alloys and 2 Cr-containing alloys.
Figure 4.5 SEM micrograph of alloy 5 (Al-6.1Zn-2.3Mg-2.6Cu), showing the main particles: S and Al$_7$Cu$_2$Fe.

Figure 4.6 SEM micrograph of alloy 6 (Al-6.7Zn-2.9Mg-1.9Cu), showing the main particles: S and T phases.
Chapter 4 Microstructure of Zr-containing and Cr-containing Alloys

Figure 4.7 SEM micrograph of B3 (Al-6.16Zn-3.02Mg-1.98Cu), showing the main particles: S and Al$_7$Cu$_2$Fe phases.

Figure 4.8 SEM micrograph of B2 (Al-5.74Zn-2.17Mg-1.52Cu), showing the main particles: Al$_7$Cu$_2$Fe phase.
Figure 4.9 DSC three runs of alloy 5 (Al-6.1Zn-2.3Mg-2.6Cu) aged at 172°C for 16h, showing the main heat effects: effect A corresponds to dissolution of \( \eta' \), effect B precipitation of \( \eta \), effect C dissolution of \( \eta \), effect D formation of S phase, effect E dissolution of S, effect F melting of T phase, effect G melting of S phase. Heating rate 10°C/min.

Figure 4.10 DSC curves of three alloys aged at 172°C for 16h, heating rate 10°C/min. 2: medium Cu and medium Mg; 5: high Cu; 6: high Mg.
Figure 4.11 DSC curve of alloy 6 at different solution treatment temperatures: 437°C and 467°C for 1h.
Figure 4.12 TEM micrograph of the Al-6.1Zn-2.3Mg-2.6Cu (alloy 5) aged for 16h at 172°C. (a) precipitates; (b) sub-grain boundaries (bright-field, B=[100]).
Figure 4.13  TEM micrograph of the Al-6.7Zn-2.9Mg-1.9Cu (alloy 6) aged at 172°C. (a) for 16 hours; (b) for 4 hours, both showing a sub-grain boundary and narrow PFZs adjacent to the boundaries (bright-field, B=[100]).
Figure 4.14 TEM micrographs of the Al-6.7Zn-2.9Mg-1.9Cu (B3) aged at 172°C for 4 hours. (a) S phase; (b) intermetallic particles with solute depleted areas adjacent to the particles (bright field, orientation is close to [110]).
Figure 4.15 Selected area diffraction pattern from sample of the Al-6.7Zn-2.9Mg-1.9Cu (alloy 6) aged for 16h at 172°C (B=[100]). The reflection of precipitates represents η phase.

![Diffraction Pattern](image)

Figure 4.16 Illustrative sketch of the diffraction pattern for B=[100], with cross-like pattern representing the reflection of η phase.
Figure 4.17 Solvi of S phase in Al-Zn-Mg-Cu with Zn=6 wt%, temperature range 440-490°C. Compositions of alloys 1, 2, 5, 6 and 9 and composition ranges for 7075 and 7050 commercial alloys are indicated.

Figure 4.18 The quaternary system Al-Zn-Mg-Cu at 460°C with 6%Zn, θ: CuAl₂, Z: Mg₂Zn₁₁, data from Ref. [Strawbridge 1948].
Chapter 5  DSC Analysis of Precipitation and Dissolution Reactions

5.1  Introduction

With the ever increasing demands put on high strength aluminium alloys for aerospace applications, improvement in alloy chemistry and thermo-mechanical treatments for optimisation of strength, toughness and stress-corrosion resistance of 7xxx (Al-Zn-Cu-Mg) alloys is an area of continued interest [Gupta et al 1998, Park and Ardell 1988, Morris et al 1997]. In order to improve understanding of how compositional variations and ageing affect precipitation, 9 Zr-containing Al-Zn-Mg-Cu alloys and a commercial 7075 alloy with different Zn, Mg and Cu contents were investigated using differential scanning calorimetry (DSC). DSC is employed to analyse the precipitation and dissolution of metastable and stable phases in these alloys, because it is sensitive to reactions of the main phases determining these properties, i.e. GP zones, η', η, T, S and Mg₃Si phase.

In this chapter, DSC scans of the 9 Zr-containing alloys in various overaged conditions are presented, and the influence of compositional factors and ageing treatments on DSC heat evolution is studied. The DSC data is used to discuss the optimisation of alloy chemistry.

5.2  Experimental Results

5.2.1  Selection of Ageing Treatment

Earlier efforts to assess the effect of composition on the balance of strength and electrical conductivity in 7xxx alloys indicated that Mg had the most significant influence on properties by strongly increasing strength and decreasing conductivity [Warner et al 1997, Pitcher 1998]. Therefore the 9 alloys were split into groups depending on their nominal Mg content for ageing trials. The specimens for tensile
test and conductivity measurement were extracted from the plates that were solution treated at 475°C for 1 hour and cold water quenched and aged by ramping at 20°C/hour to 172°C and holding at 172°C for the following times: alloys 3, 7, 8, 9 (1.9% Mg) for 1, 2, 4, 8 h; alloys 2, 4, 5 (2.3% Mg) for 2, 4, 8, 16 h; alloys 1, 6 (2.6% Mg) for 4, 8, 16, 32 h.

DSC experiments were performed on samples which were solution treated and aged at 172°C for various ageing times. These ageing treatments were selected in accordance with treatments used for the tensile test and conductivity measurement [Pitcher 1998], i.e. for alloys 3, 7, 8, 9 (1.9% Mg), the ageing times were 1h, 2h, 4h, 8h; for alloys 2, 4, 5 (2.3% Mg), the ageing times were 2h, 4h, 8h, 16h; for alloys 1, 6 (2.6% Mg), the ageing times were 4h, 8h, 16h, 32h.

5.2.2 Typical DSC Heat Effect Peaks

During DSC heating and cooling process the precipitation and dissolution reactions in the sample are reflected by a number of heat effect peaks in the DSC curves. Figure 5.1 shows a DSC curve of alloy 2 aged at 172°C for 8 hours. Earlier work by other authors [Park and Ardell 1988] evidenced that for the present overaged alloys peak A corresponds to the dissolution of η', B corresponds to the formation of η whilst peak C represents the dissolution of η. Since all alloys are in the overaged condition, formation and dissolution of GP zones and most of the precipitation of η' have been completed prior to DSC experiments and thus these reactions are not observed. Two further effects, D and E, are observed in alloy 5 (see Figure 5.2). In view of the high Cu content of this alloy, these two effects are thought to be due to the formation and subsequent dissolution of S phase. Peak G is due to the melting of S phase [Morris et al 1997] and the presence of this phase has been confirmed in the SEM/EDS experiments on alloy 5 (see previous chapter). The second type of intermetallic found was Al₃Cu₂Fe. Melting of this phase is not observed in DSC experiments because the reaction is obscured by melting of the Al matrix phase. Peak F has been observed for alloys with high Mg contents which contain T phase, and hence this peak is interpreted as being due to the melting of this Mg-rich phase.
Chapter 5 DSC Analysis of Precipitation and Dissolution Reactions

The 9 Zr-containing alloys aged at 172°C for 8 hours were studied using DSC, and the main DSC effects observed, along with an attempt at identification of these effects are summarised in Table 5.1.

Table 5.1 Identification of the main effects in DSC curves of the 9 Zr-containing alloys (aged at 172°C for 8 h)

<table>
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<th>Effects</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
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<td></td>
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<tr>
<td>1</td>
<td>η' disso.</td>
<td>η forma.</td>
<td>η disso.</td>
<td></td>
<td></td>
<td>T melting</td>
<td>S melting</td>
</tr>
<tr>
<td>2</td>
<td>η' disso.</td>
<td>η forma.</td>
<td>η disso.</td>
<td></td>
<td></td>
<td>T melting</td>
<td>S melting</td>
</tr>
<tr>
<td>3</td>
<td>η' disso.</td>
<td>η forma.</td>
<td>η disso.</td>
<td></td>
<td></td>
<td>T melting</td>
<td></td>
</tr>
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<td>η forma.</td>
<td>η disso.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>η' disso.</td>
<td>η forma.</td>
<td>η disso.</td>
<td>S forma.</td>
<td>S disso.</td>
<td>T melting</td>
<td>S melting</td>
</tr>
<tr>
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<td>η forma.</td>
<td>η disso.</td>
<td></td>
<td></td>
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<td>S melting</td>
</tr>
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<td>η forma.</td>
<td>η disso.</td>
<td>S forma.</td>
<td>S disso.</td>
<td>T melting</td>
<td>S melting</td>
</tr>
<tr>
<td>8</td>
<td>η' disso.</td>
<td>η forma.</td>
<td>η disso.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>η' disso.</td>
<td>η forma.</td>
<td>η disso.</td>
<td>S forma.</td>
<td>S disso.</td>
<td>T melting</td>
<td>S melting</td>
</tr>
</tbody>
</table>

The onset melting temperature of T and S phases has been measured and is gathered in Table 5.2. The start melting temperature of T and S phases for the 9 alloys is consistent, i.e. the melting temperature of T is about 480°C, the melting temperature of S is about 492°C.

Table 5.2 Onset melting temperature of T and S phases (°C)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<td>479.4</td>
<td>479.8</td>
<td>--</td>
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<tr>
<td>S phase</td>
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<td>492.2</td>
<td>--</td>
<td>--</td>
<td>491.1</td>
<td>491.3</td>
<td>492.7</td>
<td>--</td>
<td>492.1</td>
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</table>

5.2.3 DSC Curves and Reaction Parameters

In order to further analyse the DSC data and study the correlation between the DSC data and properties, the reaction parameters were measured from DSC curves. The parameters are peak temperature of η' dissolution $T_p$, end temperature of η' dissolution $T_e$, heat flow at 190°C HF, and heat of η' dissolution $\Delta Q$, as presented,
together with the available strength and conductivity values, in Table 5.3. An illustrative graph for measuring the thermal parameters of $\eta'$ dissolution is sketched in Figure 5.5. $\Delta Q$ was calculated by integrating the area from start temperature to end temperature $T_e$.

DSC curves of alloy 2 and 5 aged for various ageing times show that (see Figures 5.3-5.4) on increasing ageing times, the $\eta$ formation effect systematically decreases. Also on increasing ageing times the total heat of $\eta'$ dissolution increases whilst the effect shifts to higher temperatures. This is due to a combination of precipitation of $\eta'$ (which will increase the effect of $\eta'$ dissolution), growth of $\eta'$ (which shifts this effect to higher temperatures) and formation of $\eta$ (which enhances the $\eta'$ dissolution effect by reducing the overlap with the $\eta$ formation effect). It is further noted that variations in the effects that occur between 400 and $500^\circ C$ do not depend on ageing time in a systematic manner. Further to the analysis of the thermal parameters measured from DSC curves (see Table 5.3), it was found that correlations between $\eta'$ dissolution peak and conductivity and yield strength exist. Overall, $T_p(\eta')$, $T_x(\eta')$, and $\Delta Q(\eta')$ vary in a consistent manner with increasing ageing time, i.e. they all increase as ageing time increases. The conductivity also increases with ageing time, but for the present peak-aged and overaged alloys proof stress generally decreases with ageing time.
Chapter 5 DSC Analysis of Precipitation and Dissolution Reactions

Table 5.3 Heat of reactions obtained from DSC curves for 9 7xxx alloys for various ageing times at ageing temperature 172°C and the correlation to the 0.2% proof stress (at T/2) and electrical conductivity (at T/2). T_p is the peak temperature, ΔQ is the heat of dissolution, HF is heat flow.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ageing Time (h)</th>
<th>T_{eq}(°C)</th>
<th>T_{pr}(°C)</th>
<th>ΔQ at T_{pr} (J/g)</th>
<th>HF at 190°C (J/g.K)</th>
<th>σ_{0.2}PS (Mpa)</th>
<th>%IACS</th>
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</table>
5.3 Discussion

5.3.1 Effect of Compositional Variations

The influence of different Zn, Mg, and Cu contents on DSC curves of alloys aged for 8 hours are shown in Figures 5.6-5.9, respectively.

In Figure 5.6, alloy 1 has low Zn:Mg ratio and alloy 3 has high Zn:Mg ratio whilst the ratio for alloy 2 is medium. The Cu content for three alloys is constant at 1.9%. It is observed that alloy 1 with low Zn:Mg ratio presents a very sharp endothermic peak which corresponds to the melting of S phase. The heat effects of S melting decrease with increasing the Zn:Mg ratio. This result is consistent with the phase diagrams (Figures 4.17-4.18) which indicates that at the solution treatment temperature alloy 3 is in the α phase field, whilst the other two alloys are in the (α + S) phase field.

In Figure 5.7, alloy 4 and alloy 5 have medium Zn:Mg ratio and medium Mg, the Cu content of alloy 4 (1.2%) is low and that of alloy 5 (2.6%) is high. It is apparent that for alloy 5 the high Cu content results in a strong peak for S melting due to the presence of S phase [Mondolfo 1976], whilst for low Cu alloy 4, no S phase is observed. Again these observations are consistent with the phase diagrams (Figures 4.17-4.18).

In Figure 5.8, alloy 6 has high Zn+Mg content and high Mg content (2.9%), alloy 7 has low Zn+Mg content. The melting peak in alloy 6 starts at 480°C and hence the sharp endothermic peak is ascribed to T phase and S phase melting.

In Figure 5.9, it is clear that the sharp peak at 490°C for alloy 9 corresponds to S melting because of the high Cu content of the alloy, whilst for alloy 8 with low Cu content, S phase melting is not observed. Again these observations are consistent with the phase diagrams (Figure 4.17).

5.3.2 Correlation Between DSC Data and Properties

The data gathered from the DSC curves exhibit some correlations. Firstly, there is a general trend that both the heat of η' dissolution and conductivity increase significantly with increasing ageing time for all of the alloys studied, whilst the yield strength generally decreases with ageing time. To give an example, for alloy 1 and 6 the
correlation between the heat of \( \eta' \) dissolution, \( \Delta Q_{\eta'} \), electrical conductivity and ageing time is plotted in Figure 5.10. The fact that conductivity increases with ageing time was also evidenced for alloy 7475 [Hepples 1987]. A plot of conductivity against heat of \( \eta' \) dissolution \( \Delta Q_{\eta'} \) (see Figure 5.11) indicates that the conductivity increases with increasing \( \Delta Q_{\eta'} \). This is because the \( \Delta Q_{\eta'} \) reflects to some extent the amount of \( \eta' \) precipitates. The larger \( \Delta Q_{\eta'} \) value implies that the sample contains more \( \eta' \), thus more Mg and Zn has precipitated and is “tied-up” in the \( \eta' \) phase. Since alloying elements dissolved in the Al-rich phase strongly reduce its electrical conductivity [Hatch 1983], it is expected that the conductivity will go up as a result of the reduction of concentration of Mg and Zn in the matrix, which accompanies \( \eta' \) precipitation.

5.3.3 Optimisation of Alloy Composition

In terms of the balance of the main properties of 7xxx alloys (strength, toughness and SCC resistance/conductivity) the present results indicate some interesting points. Firstly, it is clear that the high Cu and high Mg alloy contain significant amounts of coarse S phase which will degrade the toughness of the alloys. Hence these compositions are ruled out for most high strength aerospace applications. Mg and Cu incorporated in S phase will have very little effect on strength and conductivity of the alloy. Further, excess Mg is known to have a strong influence on conductivity [Femminella et al 1999] (high conductivity is related to susceptibility to SCC) thus indicating that a low Zn:Mg ratio is detrimental to this property. A further consideration is that to achieve high strength, high amounts of \( \eta'/\eta \) should be able to precipitate and hence that high amounts of Mg and Zn should be dissolved in the Al-rich phase of the alloys.

To explore the optimisation of Mg and Zn contents further, we approximate the \( \eta \) phase dissolution effect by a triangle, as illustrated in Figure 5.12 (dissolution effects of equilibrium phases in many Al based alloys roughly approximate this shape, see e.g. Starink and Van Mourik 1992, Starink and Zahra 1998c). Considering that an optimised alloy should contain the maximum amount of Zn that can be dissolved at the solution treatment temperature \( T_{st} \), we can thus estimate:
\[
\frac{\chi_{Zn}^2 (\text{optimised alloy})}{\chi_{Zn}^2 (\text{alloy 2})} = \frac{\Delta Q(\text{optimised alloy})}{\Delta Q(\text{alloy 2})} = \frac{(T_{st} - T_i)^2}{(T_c (\text{alloy 2}) - T_i)^2}
\]

where \(T_{st}\) is the solutionising temperature and \(\chi_{Zn}^2\) is the gross Zn content of the alloy.

From Figure 5.12, \(T_i\) is approximated as 220°C. Using \(T_{st} = 475°C\) this estimate indicates that both the Zn and Mg content can be increased by about 12%. However, we should additionally consider that Mg (and Cu) content should remain below the S phase solvus, and hence Cu, Mg and Zn composition should be limited. Thus, in order to optimise the balance of strength-toughness-SCC resistance alloy compositions around Al-7wt%Zn-2.3wt%Mg-1.7wt%Cu should be considered. If processing can be carried out such that \(T\) phase is absent, solution treatment temperatures can be increased to just below the melting point of S phase. For \(T_{st} = 485°C\), S phase solvus is no longer a limiting factor, and the optimised composition then becomes about Al-7.9wt%Zn-2.5wt%Mg-1.8wt%Cu (Phase diagrams indicate that the presence of \(T\) phase is induced by segregation of Mg and hence increasing \(T_{st}\) to 485°C is generally only possible for thinner plate). Obviously, the present interpretations based on DSC data alone need to be verified by comparison with data on mechanical properties of a wide range of 7xxx type alloys.

5.4 Conclusions

For solution treated samples, incipient melting of S phase at 490°C was observed in DSC scans for high Cu and high Mg alloys after all ageing treatments. Incipient melting of \(T\) phase at 480°C was observed only for the alloy with high Mg and Zn contents (alloy 6).

DSC can be used to investigate the optimisation of the critical properties such as strength, toughness and stress-corrosion cracking resistance of 7xxx (Al-Zn-Cu-Mg) Al alloys by considering S and \(T\) phase content, incipient melting and amounts of \(\eta\) phase. The detailed analysis of DSC data indicates that optimised properties are obtained for Zn:Mg ratios around 3 and compositions around Al-7.3wt%-2.4wt%Mg-1.8wt%Cu.

There exists a correlation between \(\eta'\) DSC dissolution peak and yield strength and conductivity as a result of the increase in conductivity with ageing time and generally
Chapter 5 DSC Analysis of Precipitation and Dissolution Reactions

decrease in yield strength with ageing time. Concerning the precipitation of \( \eta' \), it was found that the peak dissolution temperature of \( \eta' \) increases generally with ageing time. Also the reaction heat of \( \eta' \) dissolution increases with ageing time.
Chapter 5 DSC Analysis of Precipitation and Dissolution Reactions

Figure 5.1 DSC curves of runs 1 to 3 on alloy 2 aged at 172°C for 8 hour. Heating rate: 10°C/min.

Figure 5.2 DSC curves of runs 1 to 3 on alloy 5 aged at 172°C for 8 hour. Heating rate 10°C/min.
Figure 5.3 DSC curves of alloy 2 aged for various times. Heating rate 10°C/min.

Figure 5.4 DSC curves of alloy 5 aged for various times. Heating rate 10°C/min.
Figure 5.5 Illustrative graph for measuring thermal parameters of η' dissolution.
Chapter 5 DSC Analysis of Precipitation and Dissolution Reactions

Figure 5.6 DSC curves of alloy 1, 2 and 3 aged for 8 hours. Alloy 1: low Zn(+Cu): Mg ratio; Alloy 2: medium Zn(+Cu): Mg ratio; Alloy 3: high Zn(+Cu): Mg ratio.

Figure 5.7 DSC curves of alloy 4 and 5 aged for 8 hours. Medium Zn:Mg and medium Mg. Alloy 4: low Cu, alloy 5: high Cu.
Chapter 5 DSC Analysis of Precipitation and Dissolution Reactions

Figure 5.8 DSC curves of alloy 6 and 7 aged for 8 hours. Alloy 6: high Zn+Mg; Alloy 7: low Zn+Mg.

Figure 5.9 DSC curves of alloy 8 and 9 aged for 8 hours. Alloy 8: high Zn:Mg, lower Cu; Alloy 9: high Zn:Mg, higher Cu.
Figure 5.10 Correlation between conductivity, ageing time and heat of $\eta'$ dissolution. Alloy 1: low Zn; alloy 6: high Zn, both high Mg and medium Cu.

Figure 5.11 Correlation between conductivity and heat of $\eta'$ dissolution. Alloy 1: low Zn; alloy 6: high Zn, both high Mg (2.6%) and medium Cu.
Figure 5.12 DSC curve of alloy 2 aged for 4h, together with an approximation of the heat of \( \eta \) dissolution using a triangle heat effect.
Chapter 6  
Modelling of Electrical Conductivity

6.1  
Introduction
Whilst the stress corrosion resistance of aluminium alloys is relatively difficult to be quantitatively assessed, the electrical conductivity, however, can be used as a measure of the SCC resistance. The SCC resistance has been found to increase with increasing electrical conductivity in 7xxx series alloys, particularly from (near) peak-aged (T6) to the overaged (T73) condition [Tsai and Chuang 1996, Ohnishi and Shiota 1986]. Consequently, the study of electrical conductivity of 7xxx alloys has been of key interest to industrial manufacturers as well as material researchers, with an aim to predict this property and improve the stress corrosion performance accordingly.

This chapter deals with the description of conductivity models for 7xxx aluminium alloys which are derived on the basis of physical and metallurgical principles. Four models of increasing complexity have been derived and the details of Model I, Model II and Model IV are discussed. As Model III is a simplified version of Model IV, it is not discussed in detail in this chapter. The models include some of the insights obtained from the microstructural analysis presented previously. The models are subsequently used to fit and predict the conductivity data of 9 Zr-containing 7xxx alloys and 6 Cr-containing 7xxx alloys under various ageing conditions.

As reviewed in the Chapter 2, several models or elements of models for electrical conductivity of aluminium alloys have been reported [Bratland et al 1997, Guyot and Cottignies 1996, Dorward 1999]. Apart from the physics-based models, adaptive numeric analysis [Femminella et al 1999, Femminella 2001, Starink et al 2000] and hybrid models combining the above two methods are
recently becoming the other approaches for modelling the conductivity of aluminium alloys. However, in this study we will concentrate on the physical models and apply them to available conductivity data of 7xxx alloys. Emphasis will be placed on the detailed conductivity Model IV, whilst some of the results obtained from Model I and Model II are also presented.

6.2 Derivation of Models for Electrical Conductivity

What follows is the derivation of three models (Model I, Model II and Model IV) with increasing complexity. The models adopt a newly derived kinetic expression and include some of the insights obtained from the microstructural analysis presented previously.

6.2.1 Conductivity Model I

In general, electrical conductivity of a metallic alloy is thought to be mainly influenced by the dissolved atoms. Neurofuzzy modelling [Femminella et al 1999] indicated that the conductivity of 7xxx alloys can be described linearly and additively by the following form:

\[
\sigma_M(t) = \sigma_0 + \sum_i q_i x_i(t) \quad (6.1)
\]

where \( \sigma_M \) is the conductivity of the matrix of Al alloy, \( \sigma_0 \) is the conductivity of pure aluminium, \( x_i \) are the concentration of alloying elements in the matrix phase at time \( t \), \( q_i \) are constant coefficients. For the 7xxx Al alloy, considering the three main alloying elements, this yields:

\[
\sigma_M(t) = \sigma_0 + q_{Zn} x_{Zn}(t) + q_{Mg} x_{Mg}(t) + q_{Cu} x_{Cu}(t) \quad (6.2)
\]

Based on Starink-Zahra model [Starink and Zahra 1997a, 1998b], the fraction of precipitates formed during ageing can be described by the expression:
\[ \alpha = 1 - \left[ \frac{(kt)^n}{\eta_i} + 1 \right]^{-\eta_i} \] (6.3)

where \( \alpha \) is the volume fraction, \( \eta_i \) is the impingement parameter, \( k \) is a temperature dependent factor, \( n \) is the growth exponent.

For 7xxx Al alloys, particularly in the peak aged and overaged conditions, it is widely believed that the precipitate \( \eta' \) is the main strengthening phase [Li et al 1999, Park and Ardell 1988], and \( \eta' \) has a chemical composition with Zn:Mg = 2.5 [Li et al 1999]. (Note that also Mg₄Zn₁₁Al has been proposed in the literature [Park and Ardell 1988], whilst APFIM work, which appears to be consistent and reliable, has indicated a Zn:Mg ratio of about 1 to 1.2 [Bigot et al 1996, Stiller et al 1999]. The model when fitted to the data yields best fits for Zn:Mg ~ 2.6.) According to a regular solution model, the solvus of \( \eta' \) can be calculated taking the following form:

\[ (C_{eq}(Zn))^{10} \times (C_{eq}(Mg))^{1} = C_0 \exp\left(\frac{-\Delta H}{k_B T}\right) \] (6.4)

where \( C_{eq} \) is the equilibrium concentration of alloying elements, \( \Delta H \) is the solution enthalpy of \( \eta' \), \( k_B \) is the Boltzmann's constant. From the above, it follows that the solvus curve of \( \eta' \) and the composition of the Al-rich phase in the course of the precipitation reaction can be constructed as Figure 6.1.

If the initial compositions of alloying elements are known, i.e. if the gross Mg, Zn, Cu contents \( (X_{Mg}(t=0), X_{Zn}(t=0), X_{Cu}(t=0)) \) are fixed, the final composition \( (X_{Mg}(t=\infty), X_{Zn}(t=\infty), X_{Cu}(t=\infty)) \) after completion of precipitation reaction can be calculated by finding the point where the curve and straight line intersect in Figure 6.1. We will assume that in good approximation \( \eta' \) does not contain Cu, and thus final Cu content is taken to be equal to the initial Cu content (i.e. \( X_{Cu}(t=\infty) = X_{Cu}(t=0) \)).

For simple approximation, we assume that the final Zn content is much less than the initial one and that Zn is nearly totally consumed, i.e. \( X_{Zn}(t=\infty) = 0 \). Thus, it follows:
From above analysis the concentration of alloying elements at specific time $t$ can be calculated using the following expressions:

$$X_{Mg}(t = \infty) = X_{Mg}(t = 0) - \frac{4}{10} X_{Zn}(t = 0) \quad (6.5)$$

Dial to the electrical conductivity being proportional to the concentration of alloying elements as described in equation (6.1), one can model the conductivity using the above equations (6.1) to (6.6). The parameters that need to be fitted are $q_i$, $\sigma_0$, $k$, $n$ and $\eta_i$.

### 6.2.2 Conductivity Model II

Model II is generated basically from Model I by taking account of resistivity instead of conductivity, i.e. the electrical resistivity of an Al alloy is proportional to the alloying elements dissolved in the matrix [Olafsson et al 1996, Van Horn 1967, Hatch 1983]. From this it follows:

$$\rho_M(t) = \rho_0 + r_{Zn} X_{Zn}(t) + r_{Mg} X_{Mg}(t) + r_{Cu} X_{Cu}(t) \quad (6.7)$$

where $\rho_M$ is the resistivity of matrix phase, $\rho_0$ is the resistivity of pure Al, $r_i$ are constant coefficients. The procedure for calculating the values for $x_i$ is the same as described in the model I.

It is noted from earlier research [Hepples 1987], that $\rho_0$ and $r$ values are available. Those values were used to eliminate the variables in the conductivity modelling work using model II, but the results for the fits were not satisfactory. This may be due to the complexity of the actual factors influencing the overall
conductivity, for instance the undissolved particles and impurities in the matrix. Hence, to enhance modelling accuracy we treat \( r_i \) as fittable parameters.

### 6.2.3 Conductivity Model IV

#### 6.2.3.1 Overview of the Model

This model is more complicated compared with the above two models. It takes account of the grains and solute depleted area (SDA) around the grain boundary. The conductivity of grains incorporates the effects of dissolved alloying elements, undissolved particles and precipitation. The model considers that the alloy consists of two zones: the grains and the solute depleted area (SDA) around the grain boundary. The respective conductivities of these two zones will be indicated as \( \sigma_G \) and \( \sigma_{SDA} \). We will approximate the grain by a single rectanguloid shape, with sizes \( d_L, d_T \) (L and T stand for longitudinal and transversal, respectively). The schematic graph of the structure of the alloy in the model is presented in Figure 6.2. In general, the conductivity of the grain increases with ageing time due to precipitation of solute elements from the Al-rich phase, however, the overall conductivity is further influenced by growth of the SDA around the grain boundary, which occurs due to the formation and growth of grain boundary precipitates. We will discuss these two conductivity contributions in detail below.

#### 6.2.3.2 Combining the Grain and SDA Resistivities

It is thought that the electrical resistivity of the alloy can be obtained in good approximation by considering an electrical schematic of the current flow in the T and L directions (see Figure 6.3). From Figure 6.3, it follows that for the current in the T direction:

\[
R_{nt} = \left( \frac{1}{R_G + R_{B,L}} + \frac{1}{R_{B,T}} \right)^{-1}
\]  

(6.8)

Divided by \( R_G \) yields:

\[
R_{nt}\frac{1}{R_G} = \frac{1}{R_G + R_{B,L}} + \frac{1}{R_{B,T}}
\]
From the latter equation, it follows:

\[
\frac{\sigma_{\text{tot}}}{\sigma_G} = \frac{1}{1 + \frac{R_{B,L}}{R_G} + \frac{R_{B,T}}{R_G}} \quad (6.10)
\]

where \( R_{\text{tot}} \) is the total resistivity, \( \sigma_{\text{tot}} \) is the total average conductivity, \( R_{B,L} \) is the resistivity of grain boundary in the L direction, \( R_{B,T} \) is the resistivity of grain boundary in the T direction, \( R_{B,L} \) is the resistivity of grain boundary in the L direction, and \( R_G \) is the resistivity of the grain. The effective resistivity of the grain boundary is estimated on the basis of a one-dimensional diffusion model for diffusion of one element. Diffusivity data of Zn, Mg and Cu [Mondolfo 1976] indicates that at the temperatures concerned (100-200°C) the diffusivities decrease in the order \( D_{\text{Zn}} \), \( D_{\text{Mg}} \), \( D_{\text{Cu}} \). As grain boundary precipitates will mainly consist of Zn and Mg containing ones, the diffusion of Mg is considered to be the time limiting process in the precipitation that occurs. The effective width of the solute depleted area, \( d_{\text{SDA}} \), around the grain boundary is approximately equal to \( \sqrt{D_{\text{Mg}} t} \) [Starink and Gregson 1995]. As diffusion process occurs along two sides, \( d_{\text{SDA}} \) can thus be estimated as \( 2 \sqrt{D_{\text{Mg}} t} \). The diffusion of an alloying element is calculated using the expression:

\[
D = D_0 \exp \left( -\frac{E_D}{k_B T} \right) \quad (6.11)
\]

where \( E_D \) is the diffusion energy, \( k_B \) is Boltzmann’s constant, \( D_0 \) is a constant.

The local conductivity in the solute depleted area (SDA) depends on the distance to the grain boundary (GB): at the GB, most alloying elements will move to the GB.
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precipitates, and the conductivity will approach that of pure Al, \( \sigma_0 \), but for material several times \( d_{\text{sd}} \) away from the GB, conductivity will approach the conductivity of the grains, \( \sigma_G \). The average conductivity of the SDA around the grain boundary, \( \sigma_B \), is estimated to equal the average of the initial conductivity of the grains, \( \sigma_G \), and the conductivity of pure Al, \( \sigma_0 \). We will assume that the resistance of the SDA can be characterised by an effective thickness and an average conductivity, and hence:

\[
\frac{R_{B,t}}{R_G} = \frac{d_B}{2d_{\text{sd}}(t)} \frac{\sigma_G(t)}{\sigma_{SDA}}
\]

(6.12)

6.2.3.3 Conductivity of the Grains

Conductivity of a dilute metallic alloy with precipitates is mainly governed by four factors: i) the conductivity of the pure metal (in our case the conductivity of pure Al, \( \sigma_{Al} \)), ii) the conductivity and volume fractions of the phases within the matrix, iii) the scattering of electrons by very small (nanometer sized) precipitates/zones [Guyot and Cottignies 1996], and iv) alloying atoms dissolved in the \( \alpha \)-rich phase. In the present model the factor iii) will be neglected, and thus the model is valid only for overaged alloys in which precipitates have grown to relatively large sizes.

i) Conductivity of the matrix phase - Dissolved Alloying Elements

Generally, the effect of dissolved alloying elements on the resistivity of a single phase is thought to be linear and additive (Matthiesen’s rule) [Van Horn 1967, Olafsson et al 1996]:

\[
\frac{1}{\sigma_{M}(t)} = \rho_{M}(t) = \rho_{M,p} + \sum_i r_i x_i(t)
\]

(6.13)

where \( \rho_M \) is the resistivity of the matrix phase, \( \rho_{M,p} \) is the resistivity of the pure metal, \( x_i \) is the concentration of alloying element \( i \) in the matrix phase (which is
time dependent due to precipitation that can occur), and \( r_i \) are constants. Hence, for a 7xxx type alloy:

\[
\rho_M(t) = \rho_{\text{Al}} + r_{\text{Zn}}x_{\text{Zn}}(t) + r_{\text{Mg}}x_{\text{Mg}}(t) + r_{\text{Cu}}x_{\text{Cu}}(t) + r_{\text{Zr}}x_{\text{Zr}}(t) + r_{\text{Cr}}x_{\text{Cr}}(t) + r_{\text{Fe}}x_{\text{Fe}}(t) + r_{\text{Si}}x_{\text{Si}}(t)
\]

(6.14)

where \( \rho_{\text{Al}} (=1/\sigma_{\text{Al}}) \) is the resistivity of pure Al. The procedure for calculating the values for \( x_i \) is outlined below.

**ii) Undissolved Particles**

First, we calculate the amount of the alloying elements that do not dissolve during solution treatment. Alloying elements can remain undissolved because they are incorporated in phases that are stable at solution treatment temperatures. In 7xxx this concerns mainly the S \((\text{Al}_{2}\text{CuMg})\) [Morris 1997], T \((\text{Mg}_{3}\text{Zn}_{3}\text{Al}_2\) with some Cu dissolved in it), \(\text{Al}_7\text{Cu}_2\text{Fe}\) [Warner et al 1997] and \(\text{Mg}_2\text{Si}\) phases, where the latter two are caused by impurities Fe and Si. The amounts of each phase present can be calculated/predicted using thermodynamic models [Liang et al 1997, Liang et al 1998] and/or phase diagrams [Villars et al 1995]. T and \(\text{Mg}_2\text{Si}\) are neglected because both previous work [Wert 1981] and data in the previous chapter have indicated that they are either not present or only present in limited amounts in commercial 7xxx alloys. We will use simplified thermodynamic models to calculate the amounts of S and \(\text{Al}_7\text{Cu}_2\text{Fe}\).

The solubility of Fe in Al is not significantly influenced by Cu or Mg additions and, hence, the amount of undissolved \(\text{Al}_7\text{Cu}_2\text{Fe}\) is simply calculated on the basis of the solubility of Fe in binary Al-Fe. For typical solution treatment temperatures of 7xxx alloys (460-485°C) the solubility of Fe in Al, \(c_{\text{Fe}}(T=T_{\text{sol}})\), is estimated at 0.0025 at% [Mondolfo 1976]. Consequently, the amount of \(\text{Al}_7\text{Cu}_2\text{Fe}\) present in the alloy after solution treatment is given by:

\[
y_{\text{Al}_7\text{Cu}_2\text{Fe}} = 10(x_{\text{Fe}}^* - c_{\text{Fe}}(T = T_{\text{sol}}))
\]

(6.15)
where $x_{Fe}^e$ is the gross Fe content of the alloy (the factor 10 appears because there are 10 atoms in the phase per atom of Fe). The amount of S phase is calculated using a regular solution model which was elucidated in section 2.4.5.

For the S phase the $\Delta H_{sol}(S)$ in ternary alloys has been determined before, and by combining solvus data at 460°C with $\Delta H_{sol}$ the S solvus as a function of the temperature can be estimated. The procedure for calculating the amount of S phase, $y_S$, is outlined in detail in section 2.4.5. After calculation of $y_S$ and $y_{Al7Cu2Fe}$ the fractions of the elements dissolved in the Al-rich phase after solution treatment can be obtained from:

\[
x_{Cu}(t = 0) = \frac{x_{Cu}^e - \frac{2}{10} y_{Al7Cu2Fe} - \frac{1}{4} y_S}{1 - y_{Al7Cu2Fe} - y_S}
\]

(6.16)

\[
x_{Mg}(t = 0) = \frac{x_{Mg}^e - \frac{1}{4} y_S}{1 - y_{Al7Cu2Fe} - y_S}
\]

(6.17)

\[
x_{Fe}(t = 0) = \frac{x_{Fe}^e - \frac{1}{10} y_{Al7Cu2Fe}}{1 - y_{Al7Cu2Fe} - y_S}
\]

(6.18)

\[
x_{Zn}(t = 0) = \frac{x_{Zn}^e}{1 - y_{Al7Cu2Fe} - y_S}
\]

(6.19)

and similar for Si.

The S and Al$_7$Cu$_2$Fe particles will have a conductivity which differs from the matrix and will thus influence the conductivity of the alloy. This effect is taken account of by employing the Rayleigh-Maxwell equation [Rayleigh 1892, Geiger and Walker 1991, Gupta et al 1996]:

\[
\rho_{comp} = \rho_{M} \left( 1 + 2V_p \frac{1 - \rho_M/\rho_p}{2\rho_M/\rho_p + 1} \right)
\]

(6.20)
where \( \rho_{\text{comp}} \) is the resistivity of the matrix with particles in it (i.e. the composite), \( \rho_M \) is the resistivity of the matrix phase, \( \rho_p \) is the resistivity of the particles and \( V_p \) is the volume fraction of particles. The volume fraction of the particles can be calculated from their densities, i.e. (for S phase):

\[
V_S = y_S \frac{M_M}{M_S}
\]  

(6.21)

where \( M_M \) and \( M_S \) are the atomic densities (e.g. in atoms/m\(^3\)) of the matrix of the S phase, respectively. Due to lack of data we approximate \( \rho_{S} \approx \rho_{Al7Cu2Fe} \approx \rho_{Al} \) and \( V_S \approx y_S \). It is noted that for the 7xxx alloys studied, \( y_S + y_{Al7Cu2Fe} < 0.03 \) and, hence, the intermetallics have a limited direct influence on the conductivity. The present approximations for \( \rho_S \) and \( \rho_{Al7Cu2Fe} \) will thus not significantly influence accuracy.

### iii) Precipitation

Having determined \( x_i(t=0) \), the next step is the determination of the concentrations of the elements after a very long ageing treatment, when (meta-)stable equilibrium is reached, \( x_i(t=\infty) \). In the present model, we will assume that in good approximation the composition of the precipitating phase is fixed, and hence it follows:

\[
x_i(t) = x_i(t = 0) - \alpha(t,T)[x_i(t = 0) - x_i(t = \infty)]
\]  

(6.22)

where \( \alpha(t,T) \) is the fraction transformed in the course of the precipitation reaction. In addition, we will approximate the precipitation by assuming that the precipitation in the grain is exclusively \( \eta' \) phase having a chemical composition with \( \text{Zn:Mg} = 2.5 \) [Li et al 1999]. According to the regular solution model, the solvus of \( \eta' \) can be calculated as:
Chapter 6 Modelling of Electrical Conductivity

\[
(c_{Zn})^{10} \times (c_{Mg})^4 = c_0 \exp \left( \frac{-\Delta H_{sol}^{\eta'}}{k_B T} \right) \tag{6.23}
\]

where \(c_{Zn}\) and \(c_{Mg}\) are equilibrium concentrations of alloying elements Zn and Mg, \(\Delta H_{sol}^{\eta'}\) is the solution enthalpy of \(\eta'\). We will assume that in good approximation \(\eta'\) does not contain Cu, thus after completion of precipitation reaction the Cu content is equal to the initial Cu content, i.e. \(x_{Cu}(t = \infty) = x_{Cu}(t = 0)\). For simple approximation, we further assume that the final Zn content is much less than the initial one and that Zn is nearly consumed after completion of precipitation reaction, i.e. \(x_{Zn}(t = \infty) = 0\). Thus, it follows:

\[
x_{Mg}(t = \infty) = x_{Mg}(t = 0) - \frac{4}{10} x_{Zn}(t = 0) \tag{6.24}
\]

The temperature dependent fraction \(\alpha(t,T)\) can be approximated using the Starink-Zahra expression (see section 2.5.1). Owing to the amounts transformed being temperature dependent, through the factor \(k(T)\), the overall conductivity changes are affected by the temperature. After calculation of the concentrations of individual alloying elements, the conductivity can be calculated by equation (6.13).

6.3 Conductivity Data Sets

In this study, the electrical conductivity data sets on all alloys but the 7475 alloy were provided by Qinetiq, the former Defence Evaluation and Research Agency (DERA), Farnborough, UK.

6.3.1 Dataset of Zr-containing Alloys

The available conductivity dataset of 9 Zr-containing alloys under different ageing conditions is shown in Table 6.1.
Table 6.1 Electrical conductivity of 9 Zr-containing alloys aged at 172°C (%IACS)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
<th>32</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>34.1</td>
<td>37.0</td>
<td>37.4</td>
<td>37.9</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>35.7</td>
<td>37.2</td>
<td>40.7</td>
<td>41.7</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>36.8</td>
<td>37.9</td>
<td>39.6</td>
<td>43.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>36.9</td>
<td>38.0</td>
<td>40.9</td>
<td>41.5</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>36.2</td>
<td>37.9</td>
<td>41.9</td>
<td>42.7</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>34.4</td>
<td>37.7</td>
<td>38.1</td>
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<td>37.0</td>
<td>38.0</td>
<td>39.5</td>
<td>43.1</td>
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<td>-</td>
</tr>
<tr>
<td>8</td>
<td>38.4</td>
<td>39.3</td>
<td>41.1</td>
<td>43.8</td>
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<td>-</td>
</tr>
<tr>
<td>9</td>
<td>36.4</td>
<td>37.5</td>
<td>38.9</td>
<td>43.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

6.3.2 Dataset of Cr-containing Alloys

The conductivity data of 6 Cr-containing alloys is available. Among the 6 alloys, one is the commercial 7475 alloy aged at 120°C, 150°C, 180°C, and the conductivity data is from ref. [Hepples 1987]. This dataset is shown in Table 6.2. The other 5 experimental alloys are aged at 172°C for various ageing times from 1h to 32h, and the dataset is shown in Table 6.3. For this data set conductivity was measured on small blocks of material used for age hardening curves.

6.4 Modelling of Conductivity

6.4.1 Modelling of Conductivity by Model I and Model II

Out of three conductivity models, Model I and Model II are relatively simple and straightforward. Essentially these two models abide by the similar physical principles, with only one difference. Model I assumes that the contributions of dissolved elements to the conductivity is additive and Model II assumes that the contributions of dissolved elements to the resistivity is additive (see section 6.2). In our modelling exercise, the two models were successively used to fit the conductivity data of 9 Zr-containing alloys. Figures 6.4-6.5 show the target-output (measured-modelled) scatter plots for the conductivity of 9 Zr-containing alloys using Model I and Model II. The results indicate a root mean square error (RMSE) of 0.56%IACS for Model I and 0.54%IACS for Model II. Figures 6.6-6.7 show
Chapter 6 Modelling of Electrical Conductivity

plots for the measured and modelled conductivity against ageing times for selected alloys using the two models.

It is observed from the figures that the general trends in the measured conductivity with ageing time can be fitted well using the two models. At the early stage of ageing (ageing time less than 10h) the conductivity increases relatively fast with ageing time, whilst as ageing proceeds further the curves tend to be flat. These phenomena can be interpreted by going back to the foundation of the models. As described in section 6.2, for Model I and Model II, only dissolved main alloying elements in the matrix are taken into account for calculation of overall conductivity, and the volume fraction of precipitates is calculated using the Starink-Zahra kinetic expression. In assessing these models, it was found that the best fit could be obtained with large impingement factor $\eta_i$ (>100), which indicated that Starink-Zahra expression is equivalent to the JMAK model in this case. In view of the large impingement factor it is not surprising that the resulting modelled curves reach a saturation value within a limited amount of time.

Table 6.2 Electrical conductivity of Cr-containing alloy 7475 (%IACS)

<table>
<thead>
<tr>
<th>Ageing Time</th>
<th>EC at 120°C</th>
<th>Ageing Time</th>
<th>EC at 150°C</th>
<th>Ageing Time</th>
<th>EC at 180°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>27.4</td>
<td>0.20</td>
<td>27.9</td>
<td>0.10</td>
<td>27.4</td>
</tr>
<tr>
<td>0.40</td>
<td>28.0</td>
<td>0.40</td>
<td>28.8</td>
<td>0.20</td>
<td>27.9</td>
</tr>
<tr>
<td>0.74</td>
<td>28.2</td>
<td>0.73</td>
<td>30.5</td>
<td>0.29</td>
<td>28.5</td>
</tr>
<tr>
<td>1.03</td>
<td>29.4</td>
<td>0.98</td>
<td>31.0</td>
<td>0.48</td>
<td>31.1</td>
</tr>
<tr>
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<td>1.96</td>
<td>32.3</td>
<td>0.75</td>
<td>32.7</td>
</tr>
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<td>2.18</td>
<td>29.9</td>
<td>3.37</td>
<td>32.9</td>
<td>0.97</td>
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</tr>
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<td>5.17</td>
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<td>7.35</td>
<td>33.8</td>
<td>1.94</td>
<td>35.0</td>
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<tr>
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<td>30.7</td>
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<td>34.2</td>
<td>3.00</td>
<td>37.0</td>
</tr>
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<td>25.0</td>
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<td>35.8</td>
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</tr>
<tr>
<td>100</td>
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<td>120</td>
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<td>40.8</td>
</tr>
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</table>
Table 6.3 Electrical conductivity of 5 Cr-containing alloys (%IACS)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ageing time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1</td>
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<td>4</td>
<td>27.9</td>
</tr>
<tr>
<td>5</td>
<td>28.1</td>
</tr>
</tbody>
</table>

6.4.2 Modelling of Conductivity by Model IV

Whilst Model I and Model II are relatively simple models, Model IV is more detailed, taking thermodynamics of phases into account, and thus the assessment of this model is particularly worthwhile.

The model was used to fit the conductivity data of 9 Zr-containing alloys and 6 Cr-containing alloys. To fit the model to the measured data, a number of parameters were attempted and preset on the basis of metallurgical knowledge. For instance, the Zn:Mg ratio was fixed at 2.5 (see section 6.2), kinetic exponent \( n \) was adopted as 2.5 and 0.5 for Zr-containing alloys and Cr-containing alloys respectively. This is because for the diffusion controlled reactions \( n \) needs to be integral or half integral [Cumbrera and Sanchez-Bajo 1995], and after several adjustments the best fits were obtained for the above values. The fittable parameters are the \( \sigma_0, k \) and \( r \) coefficients. The calculated conductivity was compared to the measured data and the best fits were obtained by optimizing the parameters to ensure the minimum root mean square error (RMSE). The true accuracy of the model in terms of its capability to predict “unseen data” was tested using the following procedure, generally used in adaptive numerical analysis [Bishop 1995, Haykin 1999, Geman 1992]. Training data is used to identify the modelling parameters and the test data is used to validate the model. In our modelling approach, about 80% of the total data was used to train the model, whilst about 20% of the total data was used to test the model.
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The prediction-scatter plot of conductivity for 9 Zr-containing alloys aged at 172°C is shown in Figure 6.8. The measured conductivity data contains 36 points reflecting 4 ageing times per alloy. The results indicate that the model fits well to the measured conductivity (training data) with root mean square error (RMSE) about 0.38%IACS (training error). Further assessment of accuracy of the model showed that RMSE on test data after fitting to training data is about 0.44%IACS (test error), i.e. the model maintains accuracy well and is not overfitting the training data (see section 2.7.1). Out of 9 alloys, the predicted conductivity of four alloys vs ageing time is shown in Figure 6.9. It is observed that the model can be used to fit and predict the measured conductivity data very well. Similar to the Model I and Model II, at the early stage of ageing (ageing time less than 10h) the conductivity increases quite fast, whilst, as ageing proceeds further, the curves display a slightly increasing trend with ageing time. To examine the effects of major alloying elements on conductivity of 7xxx alloys, the modelled conductivity of three alloys with different Mg contents is plotted in Figure 6.10. It is shown that with fixed Zn and Cu contents, the increase in Mg content will result in a significant decrease in conductivity.

Also the conductivity of 6 Cr-containing alloys was fitted using the model, and in total 6 alloys were considered. One of these was the commercial 7475 alloy aged at 120°C, 150°C, 180°C, and the conductivity data was from ref. [Hepples 1987]. The other 5 experimental alloys were aged at 172°C for various ageing times from 1h to 32h. This set of data contains 49 points in total. Analysis showed that the model fitted well to the measured conductivity (training data) with root mean square error (RMSE) about 0.56%IACS (training error), whilst RMSE on test data was about 0.61%IACS (test error). The prediction scatter plot of conductivity of Cr-containing 7xxx alloys is shown in Figure 6.11. The modelling results for 7475 alloy aged at three temperatures, as well as two selected experimental alloys aged at 172°C are shown in Figure 6.12 and Figure 6.13.

It is noted that for the 7475 alloy, initially data points obtained from ageing times below 1h were included in the modelling exercise. However, the modelling results were not satisfactory with a higher overall standard deviation of about 1.01%IACS. This indicates that the present conductivity model, which was derived principally on the basis of the precipitation of η’ phase, is only valid when the ageing
Chapter 6 Modelling of Electrical Conductivity

is relatively long (over 1 hour), i.e. when the precipitation is mainly due to formation of $\eta'$ rather than the formation (and dissolution) of GP zones at the earlier stage. Consequently, we eliminated the data points obtained for the ageing times less than 1.1 hour, and modelled the available 49 data points (with 30 data points from the 5 experimental Cr-containing alloys). The results show that the model can fit this conductivity data with good accuracies, as presented in Figures 6.11-6.13.

It is observed that for 7475 alloy, a high ageing temperature significantly increases conductivity (see Figure 6.12). This is attributed to the precipitation occurring faster at high temperature. The effect of alloying elements on conductivity indicates that a high concentration of alloying elements considerably reduces the conductivity of the alloy, as shown in Figure 6.13.

6.5 Discussion

6.5.1 Comparison of Conductivity Modelling of Zr-containing Alloys with Cr-containing Alloys

In the previous section, the conductivity model was used to fit conductivity data on 9 Zr-containing alloys and 6 Cr-containing alloys. The results indicated a good generalisation capability of the model, with good accuracies for both Zr-containing alloys and Cr-containing alloys. For comparison purpose, the modelling parameters obtained for the best fit to 9 Zr-containing alloys and 6 Cr-containing alloys are listed in Table 6.4.

It is obvious that the parameters obtained from the best fit are different for Cr-containing alloys and Zr-containing alloys; especially $\sigma_0$, $k$ and $n$ appear to be significantly different. There are two main causes for these differences. Firstly, Cr dissolved in the Al-rich phase has a strong direct effect on conductivity of the Al-rich phase. This is due to a combination of a substantial Cr solubility in the Al-rich phase (about 0.1 wt% at 460°C, 0.28 wt% at 550°C) and a strong reduction of conductivity per Cr atom dissolved [Hatch 1983, Hepples 1987]. This effect is reflected mainly in a different $\sigma_0$ obtained for the two types of 7xxx alloys (Table 6.4). As diffusivity of Cr is very low, precipitation of Cr during typical ageing treatments is generally not possible, and thus reduction of conductivity by Cr
appears unavoidable. The second mechanism behind the difference in modelling parameters obtained for the two types of alloys is thought to be related to the trapping of vacancies by Zr atoms. As was shown by Mukhopadhyay et al [1990] the addition of Zr to an Al-Zn-Mg alloy retards GP zone and η' formation and slows down η precipitation. This effect may explain the difference in k and n parameters obtained for the two types of 7xxx alloys (Table 6.4): a difference in k reflects a change in rate of precipitation, whilst a difference in n reflects a change in mechanism of nucleation and/or precipitation. It is believed that also Cr additions slow down precipitation and that substantial amount of Cr dissolved in the Al-rich phase is the main cause for the lower K value obtained for the Cr-containing alloys (see Table 6.4).

Table 6.4 Modelling parameters of 5 Cr-containing alloys and a 7475 alloy (49 data points), compared with 9 Zr-containing alloys (36 data points)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cr-containing alloys</th>
<th>Zr-containing alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ₀ (%IACS)</td>
<td>50.0</td>
<td>58.4</td>
</tr>
<tr>
<td>k (h⁻¹)</td>
<td>0.09</td>
<td>0.16</td>
</tr>
<tr>
<td>n</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>rₜₗₜ (%IACS⁻¹)</td>
<td>-0.23</td>
<td>-0.01</td>
</tr>
<tr>
<td>rₜₗₐₜ (%IACS⁻¹)</td>
<td>-0.25</td>
<td>-0.38</td>
</tr>
<tr>
<td>rₜₜₛ (%IACS⁻¹)</td>
<td>-0.15</td>
<td>-0.14</td>
</tr>
<tr>
<td>Zn:Mg</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>RMSE(%IACS)-training</td>
<td>0.56</td>
<td>0.38</td>
</tr>
<tr>
<td>RMSE(%IACS)-test</td>
<td>0.61</td>
<td>0.44</td>
</tr>
</tbody>
</table>

6.5.2 Validation of the Conductivity Model

In considering the validation of the conductivity model for 7xxx alloys, it is noted that the model incorporates the solute depleted area, PFZ, intermetallic particles as well as the precipitation in the grain. As presented in section 6.2, some physical principles (e.g. Matthiesen's rule and regular solution model etc.) were adopted in
Chapter 6 Modelling of Electrical Conductivity

the conductivity model, and furthermore, a novel kinetic model for precipitation transformation [Starink and Zahra 1997, 1998a,b] was used to describe the microstructural development in the alloys.

In chapters 4 and 5, microstructure analysis of 7xxx alloys revealed that ageing of 7xxx alloys is dominated by the η'/η precipitation. TEM studies of the alloys showed that the PFZs exist in the alloys and the size of PFZ is about 20-40 nm, whilst the PFZ size calculated in the conductivity model is about 20-200 nm having a wide range of the PFZs.

All the microstructure observations from the experiments as well as from available literature indicated that the microstructural features of the 7xxx alloys conform well to the basic elements of the model, which is reflected by the successful fitting of the conductivity data to the model. However, it is worth noting that the model is expected not to fit the data at very short ageing times, because the very small sizes of the precipitates will cause scattering of electrons by precipitates, which is thought to be an important mechanism influencing conductivity. Note that most overaged 7xxx alloys for commercial use are aged over 1 hour, hence, the model is applicable to the modelling of conductivity of 7xxx alloys in commercial tempers, even though it may fail for underaged alloys.

To further assess the model performance, a comparison of the accuracy of the physically based model with neurofuzzy (NF) modelling approaches was made and analysed. For Zr-containing alloys, the training error (RMSE) was 0.54%IACS and test error (RMSE) was 0.61%IACS using neurofuzzy method [Femminella et al 1999, Starink et al 2000], whilst they were 0.38%IACS and 0.44%IACS using the physically based model. The results indicate that the physically based model is more accurate than the model constructed by the NF approach. However, it should be noted that adaptive numerical modelling (including neurofuzzy modelling) has its distinct advantages, which especially appear to be outstanding for modelling problems where limited physical understanding is available, where large amounts of data are available but with some degree of noise. In these cases physically based modelling may be impossible and adaptive numerical modelling may outperform physically based modelling. On a more general note, adaptive numerical modelling has proven to be able to generalise system relationships from observational data and thereby predicting the responses of that system, and accuracy can be improved by
taking account of physical understanding prior to the modelling approaches [Femminella et al 1999, Femminella et al 2000].

Although the discussion on assessing the conductivity model appears to be reasonable, some limitations and unresolved issues should be mentioned. Firstly, it is noted that the values of $r_{\text{Mg}}$, $r_{\text{Zn}}$, and $r_{\text{Cu}}$ obtained by the fitting process (see Table 6.4) do not correspond well to the values determined for binary alloys (see appendix) as given in Ref. [Hatch 1983]. In particular the finding that $r_{\text{Mg}}$ is much larger than either $r_{\text{Zn}}$ or $r_{\text{Cu}}$ for Zr-containing alloys, thus causing the Mg content of the alloy to dominate the conductivity, is inconsistent with data for binary alloys in Ref. [Hatch 1983]. This may indicate that deviation from additivity of individual effect of alloying elements occurs, i.e. interactions between dissolved atoms could be invalidating Mathiesen’s rule (see equation 6.13). Secondly, the scattering of conducting electron by small particles was overlooked in the present model, which is thought to be critical for the conductivity in pre-aged condition [Dorward 1999]. Furthermore, the $r_{\text{Mg}}$, $r_{\text{Zn}}$, and $r_{\text{Cu}}$ coefficients are different for Cr and Zr containing alloys, which is difficult to explain and it should be noted as a limitation or imperfection of the model. However, irrespective of which mechanisms or interactions might have been overlooked in this model, it is quite clear that the model provides very good predictive capabilities and is consistent with the microstructural data presented. The model is thus valuable because of its ability to explain conductivity variations on a physical basis, and is also valuable from an industrial point of view, especially if models for other properties can be derived.

### 6.6 Conclusions

Three physically-based models for the electrical conductivity of 7xxx aluminium alloys are derived. These models include a newly derived kinetic equation for precipitation, as well as a regular solution model for the calculation of S phase solvus. Amongst the three models, Model IV is the most detailed and accurate one that takes account of grains (incorporating dissolved alloying elements, undissolved particles and precipitates), grain boundaries and solute depleted area which reflect the microstructure features of the 7xxx Al alloys. The main conclusions are as follows:
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1. For Zr-containing 7xxx alloys, 9 alloys aged at 172°C were modelled. The measured conductivity data contains 36 points with 4 various ageing times. The model fits well to the measured conductivity with root mean square error (RMSE) about 0.38%IACS for training data and 0.44%IACS for test data.

2. For Cr-containing 7xxx alloys, 5 alloys aged at 172°C and a 7475 alloy aged at three different temperatures (120°C, 150°C, 180°C) with a range of ageing times from 1h to 120h containing 49 data points were modelled. The model fits the data with RMSE about 0.56%IACS for training data and 0.61%IACS for test data.

3. The conductivity data of 7475 alloy aged under 1h was attempted to fit to the model but the results were not satisfactory. However, most overaged 7xxx alloys for commercial use are aged over 1h, hence, the model is applicable to the modelling of conductivity of 7xxx alloys in commercial tempers.

4. Cr significantly reduces the conductivity of 7xxx alloys due to the combination of significant Cr dissolving in the Al-rich phase and a strong reduction of conductivity of the Al-rich phase per Cr atom in solution.
Figure 6.1 Illustrative diagram of the Al–rich phase composition during $\eta'$ precipitation.
Figure 6.2 Schematic graph of the structure of the alloy used in the model. Grains are rectanguloids and SDA around the grain boundary provide connected paths in the shape of plates.

Figure 6.3 Schematic current flow in the T and L directions.
Figure 6.4 Measured conductivity of the 9 Zr-containing 7xxx alloys (target) at various ageing times compared with the modelled conductivity using Model I (output). RMSE equals 0.56%IACS.
Figure 6.5 Measured conductivity of the 9 Zr-containing 7xxx alloys at various ageing times compared with the modelled conductivity using Model II. RMSE equals 0.54%IACS.
Figure 6.6 Conductivity of the four Zr-containing alloys aged at 172°C vs. ageing time. Points from measured data, solid curves from Model I.
Figure 6.7 Conductivity of four Zr-containing alloys aged at 172°C vs. ageing time. Points from measured data, solid curves from Model II.
Figure 6.8 Prediction scatter plots of 9 Zr-containing alloys aged at 172°C for various ageing times (36 data points).
Figure 6.9 Conductivity of four Zr-containing alloys aged at 172°C vs ageing time. Points from measured data, open symbol for training data, solid symbol from test data, curves from the model.

Figure 6.10 Conductivity of Zr-containing alloys aged at 172°C with varied Mg contents vs ageing time. Points from measured data, open symbol for training data, solid symbol for test data, solid curves from the model.
Figure 6.11 Prediction scatter plots of 6 Cr-containing alloys, 5 alloys aged at 172°C, 1 7475 alloy aged at 3 different ageing temperatures 120, 150, 180°C (49 data points).
Figure 6.12 Conductivity of 7475 alloy aged at three temperatures 120, 150, 180°C vs ageing time, points from measured data, open symbol for training data, solid symbol for test data, curves from the model.

Figure 6.13 Conductivity of 2 Cr-containing alloys aged at 172°C vs ageing time, points from measured data, curves from the model.
Chapter 7  Modelling of Yield Strength

7.1  Introduction

The optimisation of structure-property-processing relations of high strength aluminium alloys for aerospace and automotive applications is a difficult task that can not be readily tackled without effective models and substantial modelling work. Recent published literature [Bratland et al 1997, Deschamps et al 1999a,b, Sigli et al 1996, Kolby 1996, Vermolen et al 1998] allow us to have insight into a wide variety of modelling progress for materials applications, e.g. physically based models, mathematical expressions, and adaptive numeric analysis have been developed to model complex relations such as microstructural changes, mechanical properties, industrial processes etc. In terms of property modelling of Al alloys, strength, toughness and stress corrosion resistance are thought to be three important properties for high strength Al alloys. Whilst some other researches are concerned with modelling of fracture toughness and a number of toughness models are available in the literature [Hilders and Pena 1997, Ehrstrom et al 1996, Haynes and Gangloff 1997], this work deals with modelling of strength and electrical conductivity associated with compositional variations and different ageing conditions.

In chapter 4 and 5, microstructure development with respect to composition and heat treatment conditions for 7xxx Al alloys has been analysed, and modelling of electrical conductivity in relation to stress corrosion resistance has been studied in detail in chapter 6. Modelling of yield strength of 7xxx Al alloys still remains a major target, and this is the main topic for this chapter.

As reviewed in section 2.7.4, in the light of strength modelling in Al alloys, several models or elements have been proposed by some authors over the past decade [Shercliff and Ashby 1990, Deschamps and Brechet 1999, Starink et al
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1999a], but models for yield strength of 7xxx Al alloys have not yet been reported. In this chapter, a model applicable to yield strength of Al-Zn-Mg-Cu 7xxx alloys will be described based on Shercliff-Ashby model and considerations of quaternary alloy systems, and 21 7xxx alloys with various compositions and ageing conditions will be modelled and analysed.

7.2 Models for Yield Strength of 7xxx Alloys

7.2.1 Shercliff-Ashby Model

The Shercliff-Ashby model [Shercliff and Ashby 1990] was initially developed to model the yield strength (or hardness) of a single binary or pseudo binary alloy as a function of ageing time and temperature. Subsequently the model was applied to describe the changes in yield strength due to age hardening of 6xxx aluminium alloys, but without taking the variations of concentrations of alloying elements into account. There are two variants of the model: the fixed volume fraction variant and time dependent volume fraction variant. These are described below.

1) fixed volume fraction

In general, the three contributions to the strength are considered, the intrinsic strength of the matrix $\sigma_i$, the solid solution contribution $\Delta\sigma_{ss}$, and the precipitation strengthening due to precipitation shearing ($\Delta\sigma_s$) and precipitate bypassing ($\Delta\sigma_p$) which is summed as $\Delta\sigma_{pp}$. From this, combining the contributions to the yield strength, it yields:

$$\sigma(t) = \sigma_i + \Delta\sigma_{ss} + \Delta\sigma_{pp}$$  \hspace{1cm} (7.1)

where $\Delta\sigma_{ss}$ is the function of solute concentration at equilibrium at the ageing temperature $c_0$. The solid solution contribution is taken as:

$$\Delta\sigma_{ss} = C_2c_0^{2/3}$$  \hspace{1cm} (7.2)
where $C_2$ is a constant. $c_0$ can be given out in terms of the solvus temperature and the enthalpy of solution:

$$c_0 = c_e \exp\left(-\frac{Q_s}{k_B} \left(\frac{1}{T} - \frac{1}{T_s}\right)\right) \quad (7.3)$$

where $c_e$ is the solvus boundary (the start concentration of solid solution), $Q_s$ is the free energy of solution, $T_s$ is the solvus temperature, $k_B$ is the Boltzmann constant. This equation originates from a so-called regular solution model. The details of this model are presented in Chapter 2.

In considering the isothermal ageing at fixed volume fraction, then the shape of the ageing curve is controlled by particle coarsening. If we introduce the concept 'temperature-corrected time', $P$, which is defined by:

$$P = \frac{t}{T} \exp\left(-\frac{Q_A}{k_B T}\right) \quad (7.4)$$

where $t$ is the ageing time, $T$ is the ageing temperature, and $Q_A$ is the activation energy, then the contribution due to precipitation shearing $\Delta\sigma_A$ is described as:

$$\Delta\sigma_A = C_3 f_0^{1/2} P^{1/6} \quad (7.5)$$

The contribution from the bypassing of non-shearable precipitates is given by:

$$\Delta\sigma_B = C_4 f_0^{1/2} \frac{P^{1/3}}{P^{1/3}} \quad (7.6)$$

where $f_0$ is the equilibrium volume fraction of particles, $C_3$ and $C_4$ are constants. $f_0$ is given by:
Precipitate shearing and bypassing are alternative processes, the overall contribution of precipitation to the strength is assumed to be given by:

$$\Delta \sigma_{ppt} = \left[ \frac{1}{\Delta \sigma_s} + \frac{1}{\Delta \sigma_p} \right]^{-1}$$

(7.8)

2) time dependent volume fraction

In the virtual microstructural evolution, the volume fraction of precipitates varies with the ageing, then the corresponding solid solution strength is described by:

$$\Delta \sigma_{ss}(t) = \Delta \sigma_{ss0} \left( \Delta \sigma_{ss0}^{1/2} + \Delta \sigma_{sisi}^{1/2} \right) \exp(-t/\tau_1)$$

(7.9)

where the subscripts denote initial and final values of the solid solution contribution, and $\tau_1$ is a temperature dependent factor:

$$\tau_1 = k_p T \exp(Q_a / k_B T)$$

(7.10)

And

$$\Delta \sigma_{ssi} = \sigma_q - \sigma_i, \quad \Delta \sigma_{ss0} = \sigma_{oa} - \sigma_i$$

(7.11)

where $P_p$ is the peak temperature-corrected time, which is a constant for a given ageing curve, $\sigma_q$ is the as-quenched strength, which is the sum of intrinsic strength of pure aluminium and the solution strengthening. This is a constant and some of the values for common alloys at specific temperatures are available from literature. $\sigma_{oa}$ is the overaged strength, which is the sum of the solid solution strength and the intrinsic strength of pure aluminium. The solid solution contribution to the yield
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strength can be obtained from equation (7.2)-(7.3). Then in a good approximation, the overaged strength, \( \sigma_{oa} \) is described by:

\[
\sigma_{oa} = \sigma_s + (\sigma_q - \sigma_s) \exp\left(-\frac{2Q_s}{3R} \left(\frac{1}{T} - \frac{1}{T_s}\right)\right)
\]  

(7.12)

substituting \( f_0 \) by \( f(t) \) in equations (9.5), (9.6) gives:

\[
\Delta \sigma_A = C_3 f(t)^{1/2} p^{1/6}
\]  

(7.13)

and

\[
\Delta \sigma_B = C_4 \frac{f(t)^{1/2}}{p^{1/3}}
\]  

(7.14)

where,

\[
f(t) = f_0 \cdot [1 - \exp(-t/\tau_1)]
\]  

(7.15)

By combining equations (7.1) and (7.8) the overall strength contribution at varying volume fraction can be calculated. Note that for equation (7.9), the solid solution strength \( \Delta \sigma_{ss}(t) \) decreases exponentially with ageing time, whilst the time dependent volume fraction \( f(t) \) increases with ageing time. Furthermore, equation (7.15) is a special case of JMAK kinetics in which the \( n \) equals 1. Equation (7.9) is a combination of equations (7.2) and (7.15). Thus equation (7.9) and equation (7.15) are based on JMAK kinetics. As the strength contribution due to precipitation is dominated by the volume fraction of precipitates, see equation (7.13) – (7.14), the overlap of these effects will determine the overall yield strength.

7.2.2 Modification of Shercliff-Ashby Model

As discussed in the previous section, the Shercliff-Ashby model is only applicable to a single binary or pseudo binary alloy as a function of ageing time and temperature. In order to model a range of ternary and higher order systems, some modifications need to be adopted. Specifically, modifications to take account of
compositional variations as well as ternary and higher order system need to be made in the strength model for 7xxx alloys.

1) Modification to compositional variations

In the Shercliff-Ashby approach, the final volume fraction, \( f_0 \), of precipitates during ageing is calculated. To be able to modify this to take account of compositional variations whilst still staying close to the terminology used in this model, the concept of a reference alloy will be used, i.e. an alloy with specific composition that is characteristic for the set of alloys will be considered. The final volume fraction depends on the amount of solute that remains dissolved after completion of the ageing and takes the form as:

\[
f_0 = f_{\text{max},R} \left[ \frac{c_s - c_0}{c_{s, R}} \right]
\]

(7.16)

where \( f_{\text{max},R} \) is the final volume fraction that is obtained for the reference alloy, \( c_{s, R} \) is the composition of that reference alloy, \( c_s \) is the composition of the alloy (i.e. \( c_s \) is different for each alloy), \( c_0 \) is the equilibrium (metastable equilibrium) concentration and is expressed as:

\[
c_0 = c_s \exp \left[ -\frac{Q_s}{k_B} \left( \frac{1}{T} - \frac{1}{T_{s, R}} \right) \right]
\]

(7.17)

where \( T_{s, R} \) is the solvus temperature in the reference alloy, and \( Q_s \) is the free energy of the solute. In other words, \( Q_s \) is the enthalpy of formation of the precipitate, also indicated as \( \Delta H_{\text{sol}} \).

In order to model the alloys in a range of compositions, the above two equations substitute for equations (7.3), (7.7). To derive a complete model for fixed volume fraction or varied volume fraction, the rest of equations for each case remain unaltered.
Chapter 7 Modelling of Yield Strength

For the 7xxx alloys to be considered, we can assume $c_S$ equal to the gross Zn content. We can initially assume that $Q_S \approx 30 \text{kJ/mole}$ and $Q_A \approx 100 \text{kJ/mole}$. $\sigma_i$ should have little influence on the accuracy of the model and can be chosen as 30MPa. Therefore, the model will have 5 fittable parameters: $C_1$, $C_2$, $C_3$, $C_4$ and $f_{\text{max},R}$. Note that $C_3$, $C_4$ and $f_{\text{max},R}$ can combine to give only 2 independent parameters that influence $\Delta\sigma_A$ and $\Delta\sigma_B$, so there are only 4 independent parameters to be fitted.

2) Modification to ternary and higher order system

Modelling all contributions that affect strength in a ternary or higher order system is extremely complex. For instance, solution models for this type of systems should be included in the model, and the solution strengthening due to each element should be considered separately. To date such a model has not been available in the literature. In our consideration, however, for practical purposes it may be sufficient to simplify the real situation and assume that:

$$c_S = c_A + B_B c_B + B_C c_C + \ldots \text{etc} \quad (7.18)$$

where $c_A$, $c_B$, $c_C$ are the main alloying elements and $B_B$, $B_C$ etc are fittable parameters. For 7xxx type alloys, we can apply this by taking $B=\text{Mg}$ and $C=\text{Cu}$.

7.3 Yield Strength Data Sets

The yield strength data set for 21 ZrContaining and Cr-containing 7xxx alloys under various ageing conditions is shown in Table 9.1. All the data except for 7075 alloy is available from DERA. The tensile test results were obtained from transverse half thickness ($T/2$) position. This data set contains 135 data points in total.
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7.4 Modelling Approaches / Initial Analysis

In the first stage of analysing model capability, an attempt was made to model the yield strength by separately fitting the data of 15 Zr-containing alloys and 6 Cr-containing alloys. The 15 Zr-containing alloys were modelled using the fixed volume fraction model, with 6 parameters being fixed by using experimental data and estimates: \( Q_A = 100 \text{ kJ/mole}, \quad Q_S = 30 \text{ kJ/mole}, \quad \sigma_i = 30 \text{ MPa}, \quad T_{S,R} = 196^\circ\text{C}, \quad C_{S,R} = 7.1, \) and \( C_1 = 10, \quad C_2 = 10 \) being fixed such that \( \Delta \sigma_{SS} = 55 \text{ MPa} \) on average. Subsequently, \( C_3, \quad C_4, \quad f_{\text{max},R}, \quad B_b, \quad B_c \) were optimised and a best fit with RMSE of 20.0 MPa was obtained. The available parameters were then applied to the modelling of 6 Cr-containing alloys, with only 1 fitted parameter \( C_3 \) being optimised, the other parameters were taken from the modelling of Zr-containing alloys. A very accurate fit with RMSE of 12.8 MPa was obtained. In view of this ability to model Zr and Cr containing alloys with very similar parameters, one database combining the 15 Zr-containing and the 6 Cr-containing alloys was established and an optimisation with 5 fittable parameters was performed. This yielded a good fit with a RMSE of 20.4 MPa.

In order to train and test the model, the 135 data points were split into \(~75\%\) training data and \(~25\%\) test data. After a few modelling attempts a good generalisation of the model could be obtained, with an acceptable average accuracy. The model was used in terms of fixed volume fraction and varied volume fraction, and we will present the modelling results of these two cases below.
Table 7.1 Yield strength of 21 alloys under various ageing conditions
(T/2 position, MPa)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ageing Temp</th>
<th>Ageing Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>1   2   4   8   10   16   20   29   32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>172</td>
</tr>
<tr>
<td>1</td>
<td>172</td>
<td>-    - 487/489 478/476 - 465/467 - - 444/438</td>
</tr>
<tr>
<td>2</td>
<td>172</td>
<td>-    516/513 516/510 465/464 - 450/451 - - -</td>
</tr>
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<td>3</td>
<td>172</td>
<td>513/512 511/510 502/501 424/428 - - - - -</td>
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<td>172</td>
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<td>-    - - 553 - 516 495 - -</td>
</tr>
<tr>
<td>N4</td>
<td>172</td>
<td>-    - - 550 - 521 501 - -</td>
</tr>
<tr>
<td>N5</td>
<td>172</td>
<td>-    - - 519 - 492 473 - -</td>
</tr>
<tr>
<td>N6</td>
<td>172</td>
<td>-    - - 537 - 516 501 - -</td>
</tr>
<tr>
<td>B1</td>
<td>172</td>
<td>-    429/431 418/416 - 394/394 - - -</td>
</tr>
<tr>
<td>B2</td>
<td>172</td>
<td>-    455/458 432/434 - 405/407 - - -</td>
</tr>
<tr>
<td>B3</td>
<td>172</td>
<td>-    520/517 503/501 - 434/434 - - -</td>
</tr>
<tr>
<td>B4</td>
<td>172</td>
<td>-    484/479 469/470 - 410/409 - - -</td>
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<td>B5</td>
<td>172</td>
<td>-    488/491 472/468 - 398/400 - - -</td>
</tr>
<tr>
<td>7075</td>
<td>172</td>
<td>-    493/492 476/480 462/458 - 421/419 - - -</td>
</tr>
</tbody>
</table>
7.5 Results

The modified Shercliff-Ashby model, with modification for compositional variations and ternary or high order system, was used to fit the yield strength of 217xxx alloys. Figure 7.1 shows a prediction scatter plot for 217xxx alloys using the fixed volume fraction model. The result indicates a training error of 21.0 MPa and a test error of 21.2 MPa, with 135 data points in total. The yield strength prediction plots for a range of alloys are shown in Figures 7.2-7.5.

It is observed that the trained model predicts the test data reasonably well, with RMSE of about 21 MPa. The training error and the test error are very close, which indicates that the model is not overfitting the data. From Figures 7.2-7.5 it is observed that at the early stage of ageing the strength increases very fast until peak strength is reached (after a few hours to 10 hours). As ageing proceeds further, the strength gradually goes down, which corresponds well to the established knowledge (see Figure 2.10). Modelling results also reveal that, overall, alloys with higher alloying element contents have comparatively higher yield strength. For instance, the yield strength of alloy 1 with high Mg content is larger than that of alloy 7 with low Mg content, as shown in Figure 7.2. Also alloys with higher Zn or Cu content have higher values of yield strength, as shown in Figures 7.3-7.4. This is in good accordance with the distinct strengthening contributions of three major alloying elements. Note that the magnitude of strengthening may be various due to different content of each alloying element and its different strengthening effect.

The time-dependent volume fraction model was also used to fit and predict the yield strength data of 217xxx alloys. Figure 7.6 shows the prediction scatter plot for 217xxx alloys using the model, with training error of 20.0 MPa and test error of 21.9 MPa. This accuracy is nearly the same as for the fixed volume fraction model.

The strength prediction plots of a number of alloys are shown in Figures 9.7-9.10. It is observed that alloys with higher alloying element contents have comparatively higher yield strength. These modelling results are consistent with those obtained by using fixed volume fraction model. All the prediction plots indicate that, in general, both fixed volume fraction model and time-dependent
volume fraction model fit the yield strength data well with reasonable prediction ability.

7.6 Discussion

7.6.1 Comparison of Two Model Variants

As elucidated previously, fixed volume fraction and time-dependent volume fraction are the two variants of Shercliff-Ashby model. In the fixed volume fraction model, the volume fraction of precipitates is taken as constant and quantified as the equilibrium volume fraction of precipitates. In the time dependent volume fraction model, JMAK kinetics is incorporated and used to describe precipitation kinetics. Thus the fixed volume fraction model is a simplified case of varied volume fraction model.

The fittable parameters obtained from the two model variants are listed in Table 7.2. From Table 7.2 it is shown that the parameters obtained from the best fits for fixed volume fraction and varied volume fraction variants have some common points and differences. Firstly, parameters \( C_3 \), \( C_4 \) and \( F_{\text{max},R} \) are almost identical which indicates that the two model variants include similar contributions for the precipitate shearing and bypassing processes, and the final equilibrium volume fraction of precipitates reaches the same value at the end of age hardening (\( C_3 \) corresponds to the shearing coefficient and the \( C_4 \) bypassing coefficient). \( B_b \) is twice as large as \( B_c \), indicating that the strengthening effect of Mg is far more significant than Cu. This result is in good agreement with the previous findings by other authors [Warner et al 1997, Polmear 1996]. It is noted that high Mg content (Mg>2%) is thought to be a key factor for lower SCC resistance, as ‘excess Mg’ will reduce the conductivity of the alloy [Femminella et al 1999]. The difference in \( B_b \) and \( B_c \) for the two model variants is thought to be due to the difference in kinetics adopted in these two variants: the fixed volume fraction model considers a constant precipitate volume fraction throughout, whilst varied volume fraction model considers the precipitate volume fraction to vary with ageing according to JMAK kinetics.
Table 7.2 Modelling parameters and accuracy for two model variants

<table>
<thead>
<tr>
<th>Fittable Parameters</th>
<th>Fixed volume fraction</th>
<th>Varied volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3$ ($MPa \times K \times s^{-1}$)</td>
<td>2160</td>
<td>2403</td>
</tr>
<tr>
<td>$C_4$ ($MPa \times s \times K^{-1}$)</td>
<td>4E-04</td>
<td>4E-04</td>
</tr>
<tr>
<td>$f_{\text{max},R}$</td>
<td>4689</td>
<td>4680</td>
</tr>
<tr>
<td>$B_B$</td>
<td>4.2</td>
<td>3.6</td>
</tr>
<tr>
<td>$B_C$</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td>$k_1$</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>$P_p$ ($s \times K^{-1}$)</td>
<td>-</td>
<td>1E-35</td>
</tr>
<tr>
<td>RMSE(MPa)-training</td>
<td>21.0</td>
<td>20.0</td>
</tr>
<tr>
<td>RMSE(MPa)-test</td>
<td>21.2</td>
<td>21.9</td>
</tr>
</tbody>
</table>

The results from Table 7.2 further indicate that, in general, two model variants perform in a similar way with nearly the same accuracy, but the varied volume fraction model is more complicated, having 2 more fittable parameters. From a modelling point of view, the fixed volume fraction model performs well enough, achieving the same accuracy with simple expressions. Besides, the ageing condition in our case is after the peak in the ageing curve, and at that point the volume fraction of precipitates tends to be constant. Therefore, the fixed volume fraction variant is economical, and is recommended for use for strength modelling in the overaged 7xxx alloys. Nevertheless, time-dependent volume fraction model can interpret the strengthening mechanism in terms of real microstructural changes occurring during ageing.

7.6.2 Validation of Strength Model

The strength model used in this work is based on the Shercliff-Ashby model, with significant modifications to take account of compositional variations and quaternary alloy system. A key point in this modification is the introduction of a reference alloy, which allows the model to remain close to the structure of the Shercliff-ashby model, and to be able to consider compositional variations. Note
that with the introduction of a reference alloy, two more fittable parameters ($C_{S,R}$, $T_{S,R}$) are also generated.

From the modelling results it is observed that the strength model with two variants can predict yield strength data on 15 Zr-containing alloys and 6 Cr-containing alloys very well, with average training RMSEs about 21 MPa, and test RMSEs very close to the training error, which means that the model is not overfitting the data. For comparison an adaptive numeric modelling approach [Femminella et al 2000] was applied to the 9 Zr-containing alloys, the training RMSE was similar (about 21 MPa), but the test RMSE was much higher at 29 MPa. Thus our physically based model performs better than adaptive numeric models. (As was pointed out in the conductivity modelling, adaptive numeric modelling approach has its own advantages, i.e. more ‘flexible’ in dealing with complex data sets where prior physical understanding is very limited.)

It is further worth noting that although the model is quite accurate, a few limitations should be also mentioned. Firstly, The model is derived on the basis of the original Shercliff-Ashby model which is valid for single binary or pseudo binary alloy. In our modified version of the strength model, a quaternary alloy system was taken into account by assuming that the start concentration of solid solution $c_s$ consists of contributions of individual Zn, Mg, Cu alloying elements in a linear and additive fashion. However, it is well known that the mechanism of precipitation strengthening of age hardened 7xxx alloys is ascribed to the precipitation of $\eta'$ phase [Park and Ardell 1988, Machler et al 1991], which has a composition that can depend on ageing conditions. This would be different from the simple linear relations adopted to describe the composition dependency in our model, and hence deviation could be caused in this case. Further to the possible flaws in the model, it should be noted that the original Shercliff-Ashby model only considers three main strengthening contributions in the expressions, i.e. the intrinsic matrix strength, solution strengthening and precipitation strengthening, whilst available literature [Gomiero et al 1992, Starink et al 1999a] indicate that more strengthening mechanisms should be taken into account in the strength model. For instance, it may be beneficial to include grain and subgrain strengthening, as well as dislocation density formed by prior plastic deformation in
the strength model. Obviously these mechanisms are overlooked in the present model, possibly limiting the accuracy in the present modelling of the yield strength of 7xxx alloys. On the other hand, it should also be noted that if such strengthening mechanisms are incorporated in the model, the model might become over-complex. (Note that in the strength modelling work conducted by Starink et al [1999a] the model considered all the five strengthening mechanisms and obtained a better accuracy of about 10 MPa, but only 4 Al-Li-Cu-Mg alloys and composites were modelled.) In conclusion, regardless of what kind of assumptions are made, or which type of mechanisms are adopted in the present model, from the modelling results it is clear that the model provides reasonably good capability for predicting the yield strength of complex quaternary Al-Zn-Mg-Cu 7xxx alloys and is interpretable in terms of physical metallurgy of this type of alloys. This model, in conjunction with the conductivity model presented in Chapter 6, can provide a useful tool for predicting the properties of a wide range of 7xxx Al alloys and hence it is also valuable for commercial use.

7.7 Conclusions

A new model for yield strength in quaternary heat treatable alloys has been derived on the basis of available physical models in combination with the physical metallurgy of 7xxx Al alloys. Two model variants (fixed volume fraction model and time-dependent volume fraction model) were discussed respectively. In general, both model variants fit well to data on strength of 15 Zr-containing and 6 Cr-containing 7xxx alloys with Zn content between 5.1 to 7.5, Mg between 1.9 to 2.9, and Cu between 1.2 to 2.6. The model was applied to two ageing temperatures and nine various ageing times from 1h to 32h with the best obtainable accuracy about 21 MPa. The model can provide useful predictive tools for predicting the properties of a wide range of 7xxx Al alloys, and in especially conjunction with the derived conductivity model, it is valuable in an industrial context.
Figure 7.1 Prediction scatter plot for 21 7xxx alloys, open symbols for training data, solid symbols for test data. 135 data points in total. Training error: 21.0 MPa, test error: 21.2 MPa. Fixed volume fraction model.
Figure 7.2 Yield strength prediction for alloy 1 and 7. Curves from fixed volume fraction model, points from measured data, open symbols for training data, solid symbols for test data. Alloy 1: high Mg (Al-5.1Zn-2.9Mg-1.9Cu), alloy 7: low Mg (Al-5.1Zn-1.9Mg-1.9Cu).

Figure 7.3 Yield strength prediction for alloy 8 and 9. Curves from fixed volume fraction model, points from measured data, open symbols for training data, solid symbols for test data. Alloy 8: low Cu (Al-6.7Zn-1.9Mg-1.2Cu), alloy 9: high Cu (Al-6.7Zn-1.9Mg-2.6Cu).
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Figure 7.4 Yield strength prediction for alloy 7 and N1. Curves from fixed volume fraction model, points from measured data, open symbols for training data, solid symbols for test data. Alloy 7: low Zn (Al-5.1Zn-1.9Mg-1.9Cu), alloy N1: high Zn (Al-7.5Zn-1.96Mg-1.98Cu).

Figure 7.5 Yield strength prediction for alloy B1, B3, B4 and 7075. Curves from fixed volume fraction model, points from measured data, solid symbols for training data, open symbols for test data. Alloy B1: low Zn, Mg, Cu; alloy B4: medium Zn, Mg, Cu; alloy B3: high Zn, Mg, Cu.
Figure 7.6 Prediction scatter plot for 21 7xxx alloys, open symbols for training data, solid symbols for test data. 135 data points in total. Training error: 20.0 MPa, test error: 21.9 MPa. Varied volume fraction model.
Figure 7.7 Yield strength prediction for alloy 1 and 7. Curves from varied volume fraction model, points from measured data, open symbols for training data, solid symbols for test data. Alloy 1: high Mg (Al-5.1Zn-2.9Mg-1.9Cu), alloy 7: low Mg (Al-5.1Zn-1.9Mg-1.9Cu).

Figure 7.8 Yield strength prediction for alloy 8 and 9. Curves from varied volume fraction model, points from measured data, open symbols for training data, solid symbols for test data. Alloy 8: low Cu (Al-6.7Zn-1.9Mg-1.2Cu), alloy 9: high Cu (Al-6.7Zn-1.9Mg-2.6Cu).
Chapter 7 Modelling of Yield Strength

Figure 7.9 Yield strength prediction for alloy 7 and N1. Curves from varied volume fraction model, points from measured data, open symbols for training data, solid symbols for test data. Alloy 7: low Zn (Al-5.1Zn-1.9Mg-1.9Cu), alloy N1: high Zn (Al-7.5Zn-1.96Mg-1.98Cu).

Figure 7.10 Yield strength prediction for alloy B1, B3, B4. Curves from varied volume fraction model, points from measured data, solid symbols for test data, open symbols for training data. Alloy B1: low Zn, Mg, Cu; alloy B4: medium Zn, Mg, Cu; alloy B3: high Zn, Mg, Cu.
Chapter 8 Main Conclusions and Further Work

8.1 Main Conclusions

This thesis focuses on the microstructure analysis of Al-Zn-Mg-Cu 7xxx Al alloys, the modelling of electrical conductivity associated with stress corrosion resistance and yield strength of these types of alloys. Twenty two 7xxx alloys in a wide range of compositions within the composition windows of 7010, 7x50, 7x75 aerospace alloys are involved in the study, either for microstructure analysis, or for modelling of properties, or both.

To provide an understanding of how compositional variations and ageing treatments affect the microstructural changes and characteristics of coarse intermetallic particles in 7xxx alloys, three selected Al-Zn-Mg-Cu-Zr alloys and two selected Al-Zn-Mg-Cu-Cr alloys with different Zn, Mg and Cu contents were studied. Optical microscopy, digital image analysis, SEM/EDS, TEM and DSC were employed to study grain structure, coarse intermetallic particles, precipitates in Zr-containing and Cr-containing alloys. From the microstructural analysis it has been concluded that:

1. For all the alloys investigated, optical microscopy revealed a partially recrystallised grain structure with about 20–40% recrystallised area fraction for the Zr-containing alloys and over 50% for the Cr-containing experimental alloys, and about 20% for the commercial 7075 alloy. Unrecrystallised grains show a pan-cake shape. The recrystallised area fraction of Zr-containing alloys is less than that of Cr-containing alloys, being attributable to Zr reducing recrystallisation more effectively than Cr. As recrystallisation has direct influence on yield strength and toughness of 7xxx alloys, reducing recrystallisation remains a major concern for selection of materials for aerospace applications.
2. With regard to coarse particles in the Zr-containing alloys, DSC, SEM/EDS experiments indicated that in the high Mg alloy the main coarse particles are S (Al₂CuMg) and T (Mg₃Zn₃Al₂), whilst in the high Cu alloy they are S and Al₇Cu₂Fe. The high Cu alloy has the highest volume fraction of coarse particles. Further experiments on the Cr-containing alloys indicated that the conditions for the presence of coarse particles are of little difference between Cr-containing and Zr-containing alloys, and the detected particles are mainly S phase, Al₇Cu₂Fe, as well as Cr, Fe-rich intermetallic particles.

3. Based on the DSC observations and phase diagrams, it was found that for the alloys with 1.9% Cu and Mg in excess of 2.1%, S phase is present. If Cu in excess of 1.9%, the alloys with Mg between 1.9-2.9% will also contain S phase. For solution treated samples, incipient melting of S phase at 490°C was observed in DSC scans for high Cu and high Mg alloys after all ageing treatments. Incipient melting of T phase at 480°C was observed only for the alloy with high Mg and Zn contents (alloy 6). Further analysis indicates that some compositions in the composition windows of 7050 and 7x75 type alloys will give rise to the detrimental S phase which can not be dissolved during solution treatment, and T phase is present only if Mg content approaches the high Mg end of the composition range for the 7075 alloy (2.9wt.% Mg).

4. All observations on the presence and melting of coarse intermetallic phases can be interpreted well on the basis of phase diagrams and the temperature dependent S phase solvus based on the regular solution model.

5. DSC can be used to investigate the optimisation of the critical properties such as strength, toughness and stress-corrosion cracking resistance of 7xxx (Al-Zn-Cu-Mg) Al alloys by considering S and T phase content, incipient melting and amounts of η phase. The detailed analysis of DSC data suggests that optimised properties of thin plate are obtained for Zn:Mg ratios around 3 and compositions around Al-7.3wt%-2.4wt%Mg-1.8wt%Cu.
6. There exists a correlation between η' DSC dissolution peak and yield strength and conductivity as a result of the increase in conductivity with ageing time and generally decrease in yield strength with ageing time. Concerning the precipitation of η', it was found that the peak dissolution temperature of η' increases generally with ageing time. Also the reaction heat of η' dissolution increases with ageing time.

As far as modelling of electrical conductivity and yield strength of 7xxx Al alloys are concerned, three physically-based models for the electrical conductivity of 7xxx alloys are derived based on a newly derived kinetic equation for precipitation and a regular solution model for the calculation of S phase solvus. Amongst the three models, Model IV is the most detailed and accurate one that extensively reflects the microstructure features of the 7xxx Al alloys. A model for strength in quaternary heat treatable alloys has been derived on the basis of available physical models in combination with physical metallurgy of 7xxx Al alloys. The main conclusions of the property modelling work are as follows:

1. For modelling of electrical conductivity, 9 Zr-containing 7xxx alloys aged at 172°C with ageing time from 1h to 36h containing 36 data points, and 5 Cr-containing 7xxx alloys aged at 172°C and a 7475 alloy aged at three different temperatures (120°C, 150°C, 180°C) with ageing time from 1h to 120h containing 49 data points were modelled. Modelling results indicate that the model can fit and predict the conductivity data of a wide range of 7xxx alloys very well with an accuracy better than 1%IACS (RMSE). Specifically, the model fits best to the conductivity of 9 Zr-containing alloys with training error (RMSE) about 0.38%IACS and test error (RMSE) about 0.44%IACS, and fits the data of 6 Cr-containing alloys data with training error (RMSE) about 0.56%IACS and test error about 0.61%IACS.

2. It is noted that the conductivity data of 7475 alloy aged under 1h does not fit well to the model. However, most overaged 7xxx alloys for commercial use are aged over 1h, hence, the model is applicable to the modelling of conductivity of 7xxx alloys in commercial tempers.
3. Cr significantly reduces the conductivity of 7xxx alloys due to the combination of significant Cr dissolving in the Al-rich phase and a strong reduction of conductivity of the Al-rich phase per Cr atom in solution.

4. With respect to strength modelling, two model variants (fixed volume fraction model and time-dependent volume fraction model) based on Shercliff-Ashby model were introduced. In general, both model variants fit well to the strength data of 15 Zr-containing and 6 Cr-containing 7xxx alloys with Zn content between 5.1 to 7.5, Mg between 1.9 to 2.9, Cu between 1.2 to 2.6. The model was applied to two ageing temperatures (164°C, 172°C) and nine various ageing times from 1h to 32h with the best obtainable accuracy about 21 MPa. These results indicate that the model can provide useful predictive tools for predicting the properties of a wide range of 7xxx Al alloys, and in conjunction with the derived conductivity model, it is valuable from industrial point of view.

In a general conclusion, the detailed physically based models for conductivity and yield strength of 7xxx alloys provide good capability of predicting these properties, and they provide new progress in the area of property modelling of Al-based alloys.

8.2 Further Work

From the four chapters (chapters 4, 5, 6, 7) which are concerned with the results on microstructure-property modelling and prediction of 7xxx Al alloys, it is recommended that further relevant work will include the following:

- It would be beneficial to integrate DSC data into the modelling of properties of 7xxx Al alloys. As DSC experiments are economical and reproducible, and a DSC curve contains information on precipitation reactions, there is a potential that the properties of 7xxx alloys could be modelled and predicted in terms of the DSC reaction parameters, provided the practical model is established.
• DSC analysis indicates that alloy design and optimisation could be made based on useful DSC data, but it might not be complete and accurate if it is just based on the interpretation of the DSC data alone. As a result, it needs to be verified by comparison with data on mechanical properties of a wide range of 7xxx type alloys.

• In this thesis, conductivity modelling was processed individually in terms of Zr-containing alloys and Cr-containing alloys, i.e. two programs were made in order to model the conductivity of these alloys and two group of modelling parameters were obtained. The author made an effort to model all the conductivity data of Zr-containing and Cr-containing alloys in one spreadsheet, but at the expense of increasing standard deviation (RMSE) up to 1%IACS. This is because, in contrast to Zr, Cr considerably influences the conductivity of 7xxx Al alloys. However, for conductivity models to be conveniently used in practice, it would be worthwhile to derive a single unified model that takes Cr and Zr content into account.

• Although the models for electrical conductivity and yield strength are derived and applied to 7xxx alloys, it is expected that it can also be used to model these properties of other heat treatable Al alloys (e.g. 2xxx, 6xxx alloys).

• In terms of predictive tools for predicting the properties of 7xxx Al alloys, it would be meaningful to consider toughness models for this type of alloys. Besides, in order to optimise the property balance of high strength 7xxx alloy, it will be particularly beneficial to evaluate the property balance by combining these models. Therefore, the development of toughness models and modelling of toughness of 7xxx alloys is also a relevant topic for future work.
Appendix

1) Literature data on conductivity [Hatch 1983]:

\[ r_{\text{Zn}} = 0.2276, \quad r_{\text{Mg}} = 0.4862, \quad r_{\text{Cu}} = 0.8095 \quad (\mu \Omega \cdot \text{cm/ at } \%) \]

Pure Al conductivity \( \sigma_{\text{Al}} = 63.22 \% \text{IACS} \)

2) Conversion factor

From International Annealed Copper Standard (%IACS) to SI unit:

\[
\sigma_{\text{cl}}^{\% \text{IACS}} = \frac{\sigma_{\text{cl}}^{\% \text{IACS}} (1/ \mu \Omega \cdot \text{cm})}{\sigma_{\text{Cu}} (1/ \mu \Omega \cdot \text{cm})} \times 100
\]
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