PRECIPITATION HARDENING BEHAVIOUR OF AA6111

by

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ABSTRACT

The precipitation hardening behaviour of AA6111 was investigated by: (a) a comprehensive experimental study on the relationship between thermal processing and the evolution of microstructure and properties of the alloy, and (b) integrating the acquired knowledge with the established physical theories and models to develop a new process model to predict the yield strength of the alloy during artificial aging. Two thermal processing histories were examined: (a) artificial aging of the solution treated materials and (b) artificial aging of the materials with variable levels of natural aging. The kinetics of precipitation for the solution treated material was determined using isothermal calorimetry in the temperature range of 160-220°C. A new simple analytical procedure was also introduced to obtain the kinetics of precipitation through a set of differential scanning calorimetry experiments. A new model was proposed to describe the kinetics of concurrent precipitation and dissolution of natural aging zones during artificial aging of the naturally aged materials. The kinetics for the formation of natural aging zones was also modeled. A new process model was developed to predict the yield strength of the alloy during the entire aging process. The validity of the model was verified by the excellent agreement between the predictions of the model and independent experimental results.
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NOMENCLATURE

\( a \) a constant related to the properties of the solute; also used as a constant factor

\( A \) various constants; also used as area (see text)

\( A_0 \) initial area of the reduced section of the tensile sample

\( A_{dis} \) total heat absorbed due to the dissolution of natural aging zones during the isothermal calorimetry of T4 material

\( A_{ppt} \) area under the trace for solution treated material

\( A_{T4} \) area under the trace for T4 material

\( b \) magnitude of the Burgers vector; also used as a constant factor

\( B \) a temperature dependent parameter used in defining the kinetics of dissolution of natural aging zones

\( B_0 \) a pre-exponential constant used in defining the temperature dependence of the dissolution kinetics parameter

\( c \) a proportionality constant

\( c_e \) concentration of solute in equilibrium with a particle of infinite size (i.e. the solubility limit)

\( c_i \) solid solution content of the \( i^{th} \) element in the matrix

\( C^0, C_1, C_2, \ldots \) constant factors

\( C_a \) total solute concentration in the matrix

\( C_e \) solute concentration at equilibrium at the aging temperature (solute concentration at the peak age condition)
\( C_i \) \hspace{1cm} \text{initial solute concentration in the matrix}

\( C_l \) \hspace{1cm} \text{solute concentration at the matrix-precipitate interface}

\( C_M \) \hspace{1cm} \text{solute concentrations in the matrix}

\( C_P \) \hspace{1cm} \text{precipitate composition}

\( C_{ss} \) \hspace{1cm} \text{concentration of the solute atoms in the matrix}

\( C_t \) \hspace{1cm} \text{concentration of solute in the matrix at time } t

\( \bar{C} \) \hspace{1cm} \text{average solute concentration in the matrix}

\( \bar{C}_t \) \hspace{1cm} \text{average solute concentration in the matrix at aging time } t

\( d \) \hspace{1cm} \text{average grain diameter}

\( D \) \hspace{1cm} \text{diffusion coefficient of the solute in the matrix}

\( D_0 \) \hspace{1cm} \text{proportionality constant for the diffusivity equation}

\( e \) \hspace{1cm} \text{engineering strain}

\( f \) \hspace{1cm} \text{volume fraction of precipitates}

\( f_{2y} \) \hspace{1cm} \text{volume fraction of the natural aging zones formed during two years of natural aging}

\( f_i \) \hspace{1cm} \text{initial volume fraction of the dissolving zones}

\( f_{N_{AZ}} \) \hspace{1cm} \text{volume fraction of the natural aging zones at time } t \text{ during artificial aging}

\( f_{peak} \) \hspace{1cm} \text{volume fraction of the precipitates at the peak-age condition}

\( f_r \) \hspace{1cm} \text{relative volume fraction of precipitates}

\( f_{N_{AZ}} \) \hspace{1cm} \text{relative volume fraction of the natural aging zones during artificial aging}

\( f_{sw} \) \hspace{1cm} \text{relative volume fraction of the precipitates formed during artificial aging of naturally aged materials}
\( f_{\text{na}} \)  volume fraction of the natural aging zones at the beginning of artificial aging

\( f_{\text{r}}^0 \)  relative volume fraction of the natural aging zones at the beginning of the artificial aging process

\( F \)  obstacle strength

\( F_{\text{peak}} \)  average obstacle strength at the peak age condition

\( F_t \)  tensile load

\( G \)  shear modulus

\( \Delta G \)  difference in elastic modulus between matrix and particle

\( h_{\text{nat}} \)  relative volume fraction of the natural aging zones during artificial aging of the naturally aged material (any natural aging time)

\( k \)  a constant (dimension depends on the specific relationship)

\( k_o \)  a proportionality constant

\( k_{\text{NA}} \)  a constant in the relationship of the natural aging yield stress with time

\( l \)  distance between the potential probes on the resistivity measurement sample; also used as the average length of precipitate

\( l_o \)  initial (gauge) length of the tensile sample

\( L \)  effective obstacle spacing on the slip plane

\( L_F \)  Friedel obstacle spacing

\( L_s \)  square lattice spacing

\( \Delta l \)  displacement

\( m \)  a dimensionless number less than or equal to unity

\( M \)  Taylor factor

\( n \)  a numerical exponent for JMAK relationship

\( n_a \)  number of precipitates in the reference triangle of a triangle array of obstacles
$N$  number of atoms per zone

$N_A$  number of precipitates per unit area of slip plane

$N_s$  number of particles per unit area of slip plane in a square array of obstacles

$N_V$  number of precipitates per unit volume

$P$  probability that a needle shape precipitate oriented along $<100>$ intersects a 
{111} plane

$P_i$  material response of interest

$Q, Q_A, Q_{ppt}, Q_{dis}$  an apparent activation energy

$Q_d$  activation energy for diffusion of the solutes in the matrix

$Q_s$  enthalpy of solution of the natural aging zones

$r$  radius of a spherical particle; also radius of the circular cross sectional area of 
a precipitate on the slip plane

$r_o$  an initial precipitate radius

$r_c$  average radius of precipitates at the shearable to non-shearable transition

$r_{N_{AE}}$  average radius of the natural aging zones

$r_{peak}$  average radius at the peak age condition

$r_z$  radius of a cell containing a single zone

$R$  electrical resistance; universal gas constant (see text)

$R_c$  radius of curvature of dislocation

$S$  engineering stress; also used as a microstructural variable representing the 
shape and orientation relationship of precipitate with matrix

$S_1, S_2$  internal state variable

$t$  time
\( t_0 \)  time for onset of the exothermic event in isothermal calorimetry

\( t_{dis} \)  time for completion of the dissolution process

\( t_{exp} \)  actual time recorded by the isothermal calorimeter

\( t_f \)  time to reach zero heat evolution (approximately) during isothermal calorimetry experiment

\( t_{NA} \)  natural aging time

\( t_{peak} \)  time to peak-age condition

\( t^* \)  time to maximum heat flow during isothermal calorimetry

\( T, T_1, T_2, T_3, \ldots \)  temperature

\( \Delta t \)  time interval between the onset of the exothermic event and the maximum heat flow during isothermal calorimetry

\( V_m \)  molar volume of precipitate

\( Y \)  a defined kinetic variable

\( Z \)  number density of GP zones

\( \alpha \)  a dimensionless constant; the angle between \(<111>\) and \(<100>\) directions in Al (see text)

\( \gamma \)  interfacial energy of the precipitate/matrix interface

\( \gamma_{apb} \)  antiphase boundary energy on the slip plane of an ordered precipitate

\( \Gamma \)  dislocation line tension

\( \varepsilon \)  true strain; elastic misfit parameter (see text)

\( \eta \)  a factor related to \( C_M, C_I \) and \( C_P \)

\( \varphi_c \)  the critical angle between the adjacent arms of a dislocation when it overcomes the obstacle
\( \theta_c \)  
an angle related to the dislocation-obstacle interaction (see Figure 2.5)

\( \rho \)  
electrical resistivity; also used as dislocation density (in equation 2.7)

\( \rho_a \)  
electrical resistivity coefficient for a solute

\( \rho_e \)  
contribution to electrical resistivity by solutes at equilibrium

\( \rho_i \)  
resistivity coefficient for a solute in the matrix

\( \rho_t \)  
electrical resistivity at time \( t \)

\( \rho(T) \)  
temperature dependent thermal contribution to electron scattering

\( \rho^* \)  
electrical resistivity when the precipitation reactions are complete

\( \sigma \)  
true stress

\( \sigma_i \)  
a constant stress in the relationship of the natural aging yield stress with time

\( \sigma_i \)  
initial yield stress; frictional stress of the lattice (see text)

\( \sigma_{NA} \)  
yield strength during natural aging

\( \sigma_{NAZ} \)  
contribution of natural aging zones to the yield strength

\( \sigma_p \)  
peak strength

\( \sigma_{ppt} \)  
contribution of precipitation strengthening to the yield strength

\( \sigma_{0ss} \)  
contribution of solid solution strengthening to yield strength for the as-quenched material

\( \sigma_{ss} \)  
contribution from solid solution strengthening to the yield strength

\( \sigma_t \)  
yield strength at time \( t \) during artificial aging

\( \sigma_y \)  
yield strength

\( \sigma_{ppt} \)  
contribution from the mixture of precipitates and natural aging zones to the yield strength
$\tau_c, \tau$  
critical resolved shear stress

$\tau_1, \tau_2, \tau_4, \tau_8$  
strengthening contributions to the critical resolved shear stress from obstacles with different strengths

$\xi$  
constant factor related to the size distribution of precipitates
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CHAPTER 1

INTRODUCTION

There has been a resurgence of research interests in aluminum alloys in recent years, mainly due to the increasing demand for the utilization of lighter materials in the automotive industry. The demand is driven by the desire to reduce the environmental and economic impact of the automobile on society and to meet the governmental imposed regulations. A good example of interplay between government and industry is the Partnership for a New Generation of Vehicles (PNGV) program which had a stated goal for three times increase in fuel efficiency of a family sedan. This has led to strategic partnerships between the aluminum producers and the auto industry in developing aluminum intensive vehicles as well as strong research interests in all aspects of processing, structure, properties and alloy development. Aluminum alloys have also been the primary materials used for the structural components of aircraft for its combination of light weight and other desired properties. Hence, there have been strong interests for better understanding the processing-structure-property relationships in these alloys and new alloy development for aerospace applications, as well.

The heat treatable, i.e. precipitation hardening, aluminum alloys are of special interest for the automobile outer panels, where high strength and dent resistance are required, and bumpers, where good strength and shock absorption are needed. In both cases good formability is also an important requirement. The heat treatable 6000 series Al-Mg-Si(-Cu) alloys have been the material of choice for the skin panels. They are currently used for the outer panels in a number of models such as Audi A8 and A2, General Motor's new GMC Yukon and Chevrolet Suburban and Ford's Lincoln LS. AA6111, developed by Alcan in 1983 [Fortin et al. 1983], has been
chosen for the skin panel applications by the North American auto manufacturers for having a combination of good formability and high strengthening potential. Recently, 6000 series alloys have also been considered for aerospace applications. For instance AA6013 is being used on the Boeing 777 and AA6056 is considered to replace AA2024, which is widely used for the fuselage applications [Starke and Csontos 1998, Dif et al. 1998]. The strong interests in precipitation hardening aluminum alloys, coupled with the experimental capabilities and growing efforts in developing appropriate process models for these alloys, have resulted in significant advances in these areas in recent years.

Despite the high strengthening potential of Al-Mg-Si(-Cu) alloys, processing factors such as the hold time between the solution treatment and the artificial aging processes as well as the short duration of artificial aging can seriously impede the strengthening process. The so called paint bake cycling (PBC) process, which is a thermal cycling process [Lloyd 1998] designed to provide both paint curing and precipitation hardening for the auto panels, involves a relatively short duration artificial aging process, which may be simulated in the laboratory by aging for 30 minutes at ~ 180°C. It has been reported that the natural aging process, which occurs during the hold time, has an adverse effect on the age hardening response of paint bake cycled Al-Mg-Si(-Cu) alloys, considerably limiting the final strength. It has also been proposed that solute clustering during natural aging and the possible dissolution of these clusters during artificial aging are the major factors for the deleterious effects of natural aging. However, quantitative evolution laws for the kinetics of cluster dissolution and the concurrent precipitate formation during artificial aging have not been developed. The present work has sought a comprehensive understanding on the natural aging process and its effect on the subsequent artificial aging through an integrated modeling-experimental research approach.

Further improvement of the mechanical properties of Al-Mg-Si-Cu alloys, by exploiting their high potential for strengthening, and optimization of processes are needed to meet more
demanding requirements in the future. This in turn necessitates a better understanding of processing-structure-property relationships in these types of alloys as well as sensible process models that can provide strong predictive tools for property and process optimization and new directions for alloy development. Hence, the present work has aimed at obtaining a thorough knowledge of the precipitation hardening behaviour as well as developing a new process model for Al-Mg-Si-Cu alloy 6111 based on the acquired knowledge and well established physical theories.

The introduction of the idea of process modeling for aluminum alloys by Shercliff and Ashby [1990] has been a significant addition to the field of physical metallurgy, paving the way for subsequent process modeling work. As the knowledge on the processing-structure-property relationships in aluminum alloys has continuously increased, more and more realistic microstructural evolution laws have been incorporated into the process models. As a continuation of this trend, the present work aims at consolidating the knowledge obtained on the characteristics of the microstructure and its thermal history dependent evolution in AA6111 into a new process model. The results of the present work will have significant contributions to the field of process modeling in aluminum alloys as well as the knowledge of the precipitation hardening behaviour of Al-Mg-Si(-Cu) alloys, enriching the fundamental understandings and providing useful information for the industrially relevant process and property optimization. The process model will also be expanded for non-isothermal and multi-step aging histories in the future, so that industrially related applications can be examined.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the history of precipitation hardening will be briefly reviewed. Then an overview of the previous studies on the precipitation hardening behaviour in Al-Mg-Si(-Cu) alloys will be presented. The kinetics of isothermal precipitation and dissolution, which are pertinent to the present work, will be reviewed next. Strengthening mechanisms in aluminum alloys, in particular the theories for precipitation hardening will be described. Finally, the subject of process modeling in aluminum alloys will be surveyed.

2.2 Historical Review of Precipitation Hardening

The history of precipitation hardening studies dates back to the early years of the 20th century, when the observed change in strength with time at room temperature in aluminum alloys [Wilm 1911] was related to precipitation of a new phase [Merica et al. 1920]. Since those early years, numerous reviews on precipitation hardening have been published, including the classic review of Kelly and Nicholson [1963] as well as more recent reviews of Brown and Ham [1971], Gerold [1979], Martin [1980], Ardell [1985] and Lloyd [1985].

While, the focus of the early works on precipitation hardening was on the precipitation mechanisms [e.g. review by Mehl and Jetter 1940], the introduction of the concept of dislocation interactions with precipitates by Mott and Nabarro [1940] and the theory of non-deformable particles by Orowan [1948], shifted the emphasis to the strengthening mechanisms, resulting in enormous progress in developing theories and understanding the precipitation hardening.
phenomena. Later, the application of transmission electron microscopy (TEM) in precipitation hardening studies [e.g. Castaing 1955, Nicholson and Nutting 1958] provided the possibility of direct observation of dislocation-precipitate interactions [Kelly and Nicholson 1963]. The continuous development of microscopy techniques, including the high resolution electron microscopy (HRTEM) and atom probe field ion microscopy (APFIM) as well as the other advanced microstructural characterization techniques, such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS), along with the theoretical developments on precipitate-dislocation interactions have provided tremendous advancement in this field of study, especially in recent years.

### 2.3 Precipitation Hardening Behaviour of Al-Mg-Si(-Cu) Alloys

#### 2.3.1 History

The first studies of precipitation in Al-Mg-Si alloys have been reported by Geisler and Hill [1948] and Guinier and Lambot [1948] who using X-ray technique detected needle-shape zones in artificially aged alloys. Using the same technique, Castaing and Guinier [1949] further postulated that the needles thicken to rods and finally transform to the plate-like structure of Mg$_2$Si. In a later work, using an X-ray technique, Lutts [1961] showed that the needle-shape GP zones\(^1\) probably formed in at least two steps. The so-called “primitive zones”, which formed during the early stages, seemed not to possess any internal periodicity and it was suggested that they contain a high vacancy concentration [Lutts 1961]. Using an electrical resistivity measurement technique, Panseri and Federighi [1966] studied the pre-precipitation/clustering processes in an Al-Mg-Si alloy. As a result of these studies, they suggested that a high bonding energy exists between clusters/GP zones and vacancies and the internal structure of these zones

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\(^1\) These types of zones were called GP zones referring to the first detection of them by independent X-ray studies of Guinier and Preston in 1938.
improves continuously during aging. They also suggested that the zones formed during natural aging, are responsible for retarding any subsequent artificial aging.

The first electron microscopy studies on Al-Mg-Si alloys have been reported by Thomas [1961-1962], who suggested the aging sequence of: needles → rods → plates in Al-Mg-Si alloys. Since then numerous microscopy works in these alloys, including Cu bearing Al-Mg-Si alloys have been reported. The revived interests in these alloys as well as the development of microscopy techniques, including atomic resolution microscopy, have resulted in significant understanding of the precipitate structure, precipitation mechanisms and precipitate-dislocation interactions in these alloys. In several recent investigations, combinations of microstructural characterization methods, such as TEM, HRTEM, differential scanning calorimetry (DSC) and APFIM, have been used. The most recent findings in microstructural evolution in these alloys will be presented in the next section.

The early works on the precipitation hardening of Al-Mg-Si(-Cu) alloys, including the studies on the effect of thermal history on the microstructure as well as the age hardening response, have been reported by Pashley et al. [1966] and Pashley et al. [1967]. Since then there have been numerous studies on the mechanical behaviour and the processing-structure-property relationships in these types of alloys, many of which will be cited in the following sections and chapters.

2.3.2 Precipitation Sequence

Extensive information on the precipitation processes and sequences in Al-Mg-Si(-Cu) are available in the literature. In this review, only those recent studies that are particularly related to the present work will be summarized. Unfortunately, there are considerable discrepancies in the literature on precipitate formation in these alloys, partly due to the complexity of the
precipitation sequence and partly due to different nomenclature used by different authors. The following will try to distill the present state of knowledge.

Recent research reports suggest that the precipitation sequence in Al-Mg-Si-Cu alloys is dependent on the chemistry of the alloy, in particular the Mg:Si ratio and the concentration of Cu [Miao and Laughlin 2000a, Murayama et al. 2001]. Lloyd et al. [2000] have proposed that the precipitation sequence in AA6111 can be presented as:

Clusters/GP zones $\rightarrow \beta'' + Q \rightarrow$ equilibrium $Q + Mg_2Si$

The most recent HRTEM results have shown images for the clusters formed during natural aging in AA6016\(^1\) [Zhuang et al. 2001] and an Al-Mg-Si alloy (Al-1.6%Mg\(_2\)Si) [Matsuda et al. 2000]. Murayama et al. [2001] have also shown TEM images evidencing the formation of very fine precipitates after 7 days of natural aging in an Al-Mg-Si-Cu alloy\(^2\). The precipitates have found to be fully coherent with the matrix and have no distinct structure. Evidence for the formation of co-clusters of Mg-Si atoms, as well as clusters of Mg and Si, during natural aging has also been generated by three-dimensional atom probe (3DAP) studies on Al-Mg-Si alloys [Murayama and Hono 1999]. In addition, through combined atom probe and DSC studies on AA6061\(^3\), Edwards et al. [1998], have shown evidence for clusters of Mg, Si and Mg-Si associated with the first exothermic peak (centered at ~ 70°C) on the DSC thermogram. Figure 2.1(a) shows the DSC trace for the as-quenched AA 6111 [Lloyd et al. 2000]. The first exothermic peak on this trace (centered at ~ 90°C) is also suggested to correspond to the formation of Mg-Mg, Si-Si and Mg-Si solute clusters [Lloyd et al. 2000]. Although some details of these reactions may not be fully known, it is now generally accepted that the initial stages of the decomposition process at low temperatures involve the clustering of Mg and Si atoms.

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\(^1\) Chemical composition: 0.43% Mg, 1.2% Si, 0.15% Cu
\(^2\) Chemical composition in at%: 0.61Mg-1.22Si-0.39Cu
\(^3\) Chemical composition in wt%: 0.80 Mg-0.79Si-0.18Cu
Figure 2.1 – DSC thermograms for (a) as-quenched and (b) naturally aged AA6111.

DSC traces are shown unitless to illustrate temperature position of peaks (heating rate 10°C/min)

[Lloyd et al. 2000].
followed by the formation of Mg-Si co-clusters. It is worth mentioning that in the present work the terms “zones” and “clusters” are used as synonyms in defining the precipitates formed during natural aging, to reflect the usage in the literature.

Considering later stages of aging, combined atom probe-TEM studies on Al-Mg-Si alloys [Edwards et al. 1998 and Murayama and Hono 1999] have provided evidence for the formation of precipitates with unknown crystal structure for extended aging at a relatively low temperature (70°C) or short time aging at higher temperatures (10 minutes at 175°C, Edwards et al 1999). These types of precipitates have been reported as very fine precipitates (~ 2 nm) with no well-defined shape and fully coherent with the matrix [Murayama and Hono 1999]. Following Dutta and Allen [1991], who first reported the presence of this type of precipitate on the DSC trace for 6061, Murayama and Hono [1999] have designated these precipitates as spherical GP zones. Edwards et al. [1998] and Murayama and Hono [1999] have suggested that these types of precipitates are similar in nature to the co-clusters formed in the earlier stage of aging, however they have a higher solute concentration. The results of an in-situ aging atomic resolution microscopy on a pre-aged AA6016 alloy have also provided direct evidence for the presence of small (2.5-3 nm in diameter) circular/elliptical precipitates, with unresolved crystal structure, during aging at 175°C [Bryant et al. 1998]. These precipitates have similarly been designated as spherical GP zones [Bryant et al. 1998]. Finally, the 3DAP-TEM studies by Murayama et al. [2001] on a Cu bearing alloy have also shown that spherical GP zones are present in the microstructure of samples artificially aged for 30 minutes at 175°C after being pre-aged or naturally aged. Murayama et al. [2001] indicate that there is no enrichment of Cu for spherical GP zones, and suggested that the chemical nature of the zones is the same as that of the alloys studied by Murayama and Hono [1999] and Edwards et al. [1998]. In the case of AA6111,

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1 Chemical composition in at%: 0.61Mg-1.22Si-0.39Cu
Bryant [1999] have observed fine elliptical-shape precipitates in the microstructure of a sample heated to 245°C (10°C/min) after being pre-aged. These precipitates have been reported to coexist with the needle-shape and lath-shape precipitates for this aging condition. These precipitates have also been associated with the small DSC exotherm prior to the onset of \( \beta'' \) (needle-shape) precipitation on the DSC trace of the pre-aged AA6111 [Bryant 1999]. Similarly, a distinct exothermic effect on the DSC trace for the as-quenched AA6111 (small wide peak in the temperature range of 150-200°C, Figure 2.1(a), has been attributed to the formation of GP zones [Lloyd et al. 2000].

Proceeding now to a more advanced stage of aging, TEM studies on AA6111 have shown the presence of needle-shape precipitates along \( \langle 100 \rangle_{\text{Al}} \) in the microstructure of samples artificially aged immediately after solution treatment [Miao and Laughlin 2000b], after natural aging [Perovic et al. 1999] and after pre-aging [Bryant 1999, Miao and Laughlin 2000b]. The needle-shape precipitates in AA6111 has been identified as \( \beta'' \) [Perovic et al. 1999, Bryant 1999, Miao and Laughlin 2000b], which is a monoclinic structure containing Mg and Si \( (\text{Mg}_6\text{Si}_6) \) [Andersen et al. 1998]. The exothermic peak centered at \( \sim 245°C \) on the DSC trace of the as-quenched AA6111 has also been identified as \( \beta'' \) [Miao and Laughlin 2000c]. Through combined DSC-hardness studies, Lloyd et al. [2000] have shown that the maximum hardness is associated with the end temperature for the peak associated with \( \beta'' \) precipitation (Figure 2.1).

Perovic et al. [1999] have shown that \( \beta'' \) coexist with lath-shape precipitates, in the microstructure of samples that have been artificially aged for 0.5, 1.5 and 11 hours at 180°C after natural aging for 2.5 weeks. Similarly, Gupta et al. [2000] have observed needle-shape and lath-shape precipitates in the microstructure of AA6111 sample aged for 168 hours at 180°C. Needle-shape and lath-shape precipitates have also been reported in the microstructure of other Al-Mg-Si-Cu alloys such as 6061 [Dumolt et al. 1984], 6056 [Vivas et al. 1997a] and 6022
[Miao and Laughlin 2000a]. The lath-shape precipitates have been suggested to have hexagonal crystal structures [Dumolt et al. 1984, Chakrabarti et al. 1998, Edwards et al. 1998, Perovic et al. 1999, Miao and Laughlin 2000a, Weatherly et al. 2001]. Although there is agreement in the literature on the designation of β₁ for the needle-shape precipitate, there has been different designations for the lath-shape precipitate [Dumolt et al. 1984, Sagalowicz et al. 1994, Chakrabarti et al. 1998, Edwards et al. 1998, Perovic et al 1999, Miao and Laughlin 2000a, Weatherly et al. 2001]. The main discrepancy other than nomenclature is whether the lath-shape phase forms initially as a pre-cursor of the equilibrium quaternary Q phase and then transforms to equilibrium Q at the later stages or higher temperatures, or these phases are essentially identical to the equilibrium Q phase. The Q phase has been reported to have a quaternary composition (e.g. 33% Mg, 27%Si, 21%Cu, 19%Al in wt%, according to Weatherly et al. 2001, 31.1%Mg, 27%Si, 20.3%Cu, 21.6%Al in wt% according to Miao and Laughlin 2000a, and 35.1%Mg, 31.5%Si, 20.4%Cu, 13%Al in wt% according to Wolverton 2001. Note: the compositions in the original papers have been converted to wt% for easy comparison).

Through a combined TEM-DSC work on 6022¹, Miao and Laughlin [2000a] have shown that lath-shape precipitates are present for samples ramp heated to two different temperatures which simulate the end temperatures of two distinctive DSC exothermic peaks centered at ~280°C and ~380°C, respectively, Figure 2.2. They have found that the lath-shape precipitate associated with the former peak has a different habit plane from that of the lath-shape precipitate associated with the peak centered at ~380°C. Miao and Laughlin [2000a] have identified the precipitates associated with the peak centered at ~280°C as a pre-cursor of Q, i.e. Q’, and the one associated with the peak centered at ~380°C as equilibrium Q phase. The peak centered at ~380°C, which is a wide peak starting at ~340°C, has been shown to be associated with the

¹ Chemical composition in wt%: 0.55Mg-1.26Si-0.91Cu
Figure 2.2 – The DSC thermogram of AA6022, taken at a scan rate of 10°C/min (the exothermic peaks are shown downward). *After Miao and Laughlin 2000a.*
precipitation of Q and Si (recalling that the alloy has a high concentration of Si). In addition, using a set of DSC-TEM studies on AA6111, Miao and Laughlin [2000c] have designated the exothermic peak centered at ~ 300°C as the Q' phase. Finally, recent analytical microscopy work on Al-Cu-Mg-Si alloys (4%Cu), has identified two precursor phases, namely QP and QC, for the equilibrium Q phase [Cayron and Buffat 2000].

2.3.3 Age Hardening in AA6111

The age hardening response of AA6111 has been the subject of several studies in the past few years [Gupta et al. 1996, Poole et al. 1997, Lloyd and Gupta 1997, Lloyd 1998, Bryant 1999, Miao and Laughlin 2000b, Lloyd et al. 2000]. The areas of interest have included the natural aging response, artificial aging response of the naturally aged material as well as pre-aging and its effect on the improvement of the subsequent age hardening. It has been found that the natural aging kinetics of the alloy can be described by an equation of the form:

\[ \sigma_{NA} = \sigma_1 + k_{NA} \log t \] (2.1)

where \( \sigma_{NA} \) is the yield stress after time \( t \) at room temperature and \( \sigma_1 \) and \( k_{NA} \) are constants [Lloyd and Gupta 1997]. Attempts have also been made to obtain the artificial aging kinetics of the T4 and pre-aged material [Gupta et al. 1996, Lloyd and Gupta 1997]. Kinetic relationships have been obtained in the following form:

\[ Y = 1 - \exp\left\{ \left(\frac{\sigma_1 - \sigma_f}{\sigma_p - \sigma_i}\right)^a \right\} \] (2.2)

where \( Y \) is defined as:

\[ Y = \frac{\sigma_f - \sigma_i}{\sigma_p - \sigma_i} \] (2.3)

\( \sigma_f \), \( \sigma_i \) and \( \sigma_p \) are the yield stress at time \( t \) during artificial aging, initial yield stress and the peak strength, respectively [Gupta et al. 1996, Lloyd and Gupta 1997].
All related studies have shown that natural aging has deleterious effects on the artificial aging response of the alloy. This effect has been attributed to the cluster/GP zone formation during natural aging. It has also been indicated that the dissolution of these clusters/zones may be responsible for the slower age hardening and/or small paint bake response (PBR) of the naturally aged material [Poole et al. 1997, Lloyd 1998, Miao and Laughlin 2000b, Lloyd et al. 2000].

The enhanced artificial aging response of pre-aged materials (compared to that of the naturally aged material) has been well documented [Gupta et al. 1996, Jin et al. 1997, Lloyd 1998, Bryant 1999, Miao and Laughlin 2000b, Lloyd et al. 2000, Esmaeili et al. 2001]. Although the details of the industrial pre-aging processes are not published [Gupta et al. 1996, Lloyd 1998, Bryant 1999], laboratory pre-aging heat treatments are usually performed at an intermediate temperature range (e.g. 60-120°C) immediately after solution treatment at ~ 560°C [Miao and Laughlin 2000b, Esmaeili et al. 2001]. The enhanced artificial aging response of the pre-aged materials are usually attributed to the formation of more fully developed/larger size precipitates during pre-aging that may act as nuclei for further precipitation processes during artificial aging [Gupta et al. 1996, Lloyd 1998, Miao and Laughlin 2000b, Lloyd et al. 2000, Esmaeili et al. 2001].

### 2.4 Kinetics of Isothermal Precipitation

For isothermal transformations involving nucleation and growth processes, precipitation kinetics may be expressed by the Johnson-Mehl, Avrami, Kolmogorov (JMAK) model [Johnson and Mehl 1939, Avrami 1939, 1940 & 1941, Kolmogorov 1937, Christian 1975, Porter and Easterling 1981, Doherty 1996] with the general form of:

\[
f_r = 1 - \exp(-kt^n)
\]  

(2.4)
where \( f_r \) is the fraction transformed, i.e. the relative volume fraction of precipitates, during aging time \( t \), \( n \) is a numerical exponent independent of temperature, provided that there is no change in the nucleation mechanism and \( k \) is a temperature dependent constant whose value strongly depends on both nucleation and growth rates. The values which may experimentally be obtained for \( n \) are related to the particular nucleation and growth conditions; similar values may be obtained for different mechanisms [Christian 1975, Doherty 1996]. For the diffusional controlled growth \( n \) is 0.5-2.5, in particular \( n = 1 \) for the growth of needles and plates of finite long dimensions, small in comparison with their separation [Christian 1975, Doherty 1996].

For applying equation (2.4), a plot of \( \ln \ln \left( \frac{1}{1 - f_r} \right) \) vs. \( \ln t \) should give a straight line, whose slope and intercept with the y-axis are \( n \) and \( k \), respectively. In practice, however, the value of \( n \) is not constant, but changes continuously with time as the precipitation reactions proceed [Cahn 1956, Bratland et al. 1997]. This change is attributed to the changes in the nucleation rate. While, the constant slope, i.e. \( n \), following the initial transient effects, is considered for the steady-state nucleation rate, the subsequent decrease in the slope is attributed to the saturation of the nucleation sites [Bratland et al. 1997, Cahn 1956, Christian 1975]. Although the JMAK kinetics model may not provide a complete understanding of the mechanisms of transformation (nucleation and growth), it is of value in depicting a simple picture of the kinetics of the overall transformation process [Doherty 1996].

Some of the recent experimental methods to estimate the kinetics of precipitation in Al alloys include electrical resistivity measurement for an Al-Li-Cu-Mg alloy [Luo et al. 1993] and an Al-Li-Cu-Ag-Zr alloy [Hirosawa et al. 1998], differential scanning calorimetry (DSC) for Al-Li-Cu-Mg alloys [Starink et al. 1999a], isothermal calorimetry for Al alloys 319 and 2124 [Smith 1997, 1998a, 1998b & 1998c], as well as Al-Si and Al-Mg alloys [Starink and Zahra 1998 & 1999] and elastic modulus development for an Al-Cu-Mg alloy [Schmidt and Schmidt 2000].
Tensile [Gupta et al. 1996] and hardness [Schmidt and Schmidt 2000] test results have also been used to evaluate the evolution of the relative volume fraction of precipitates in AA6111 and an Al-Cu-Mg alloy, respectively. The above studies have mainly used modified forms of the JMAK kinetic model to describe the experimental results. Small angle X-ray scattering (SAXS) has also been used to obtain the kinetics of phase transformation in some aluminum alloys (e.g. see Guyot and Cottignies [1996] for AlZnMgCu alloys and Werenskiold et al. [2000] for an Al-Zn-Mg alloy).

Recently theoretical models, based on the established theories for nucleation, growth and coarsening mechanisms, have been developed to predict the precipitation kinetics in an Al-Zn-Mg [Deschamps and Brechet 1999] and Al-Mg-Si alloys [Vasiliev et al. 1997, Myhr et al. 2001]. These precipitation models have been incorporated in the accompanied process models to predict the yield strength of the alloys during aging processes [Deschamps and Brechet 1999, Vasiliev et al. 1997, Myhr et al. 2001].

2.5 Kinetics of Precipitate Dissolution

The kinetics of dissolution of clusters/zones during artificial aging is of interest for the present work. Therefore, a brief related background is presented in this section.

Theoretical models have been developed to describe the diffusion-controlled dissolution of a second phase particle in an infinite matrix [Aaron 1968, Whelan 1969, Aaron and Kotler 1971]. The schematic presentations of the concentration profile and the time evolution of the concentration fields around a dissolving precipitate are shown in Figure 2.3. The distinction between growth and dissolution processes, in terms of the evolution of the concentration field around the precipitate, is also shown in Figure 2.3. These theoretical models have been formulated for a single isolated precipitate in an infinite matrix. Although there may be many
Figure 2.3 – (a) Solute concentration profile around a dissolving precipitate. (b) Schematic comparison between precipitate growth and dissolution for the evolution of the concentration fields around the precipitate [Aaron and Kotler 1971].
systems that the diffusion fields of individual precipitates do not overlap during most of the dissolution process, attempts have been made to apply the models to those systems that have finite matrices [Tanzilli and Heckel 1968, Nolfi et al. 1969, Aaron and Kotler 1971]. Accordingly, the so-called “cell concept” has been introduced [Nolfi et al. 1969]. According to this concept, the precipitates have equal radii and are uniformly spaced in the matrix as shown in Figure 2.4. The cell concept has provided a reasonable framework for diffusion models that can describe dissolution processes [Aaron and Kotler 1971]. Myhr and Grong [1991] have used this concept for modeling the kinetics of dissolution for β” precipitates in 6082-T6 at high temperatures.

Aaron and Kotler [1971] have considered the Gibbs-Thomson effect in their model for dissolution of spherical precipitates. They have shown that the curvature effects slightly increase the dissolution rate at long times, emphasizing that for the precipitates larger than 1µm in radius this effect is negligible. Although, Aaron and Kotler [1971] have not shown the effect of curvature on the dissolution rate of very small size precipitates, the acceleration of dissolution due to this effect is considered important for these precipitates [Doherty 1996].

Recently, numerical models have been developed to describe the dissolution kinetics in binary and ternary alloys, relaxing some of the restrictions of the analytical models and/or expanding the applicability of the dissolution models to more realistic problems [Tundal and Ryum 1992a & 1992b, Vermolen and van der Zwaag 1996, Vermolen et al. 1998a & 1998b, Chen et al. 1999].

2.6 Strengthening Mechanisms in Aluminum Alloys

Precipitation Hardening

The precipitation of second-phase particles in the matrix cause significant strengthening in Al alloys. Due to its importance in the present work, this strengthening mechanism will be
Figure 2.4 – Two-dimensional presentation of cell concept [Nolfi et al. 1969].
discussed in more details after a review of other relevant strengthening mechanisms (section 2.6.2).

**Solid Solution Strengthening**

The contribution from solid solution strengthening, $\sigma_{ss}$, to the yield strength is given to a close approximation by [Nabarro 1967, Labausch 1970, Shercliff and Ashby 1990]:

$$\sigma_{ss} = a \bar{C}^{2/3}$$  \hspace{1cm} (2.5)

where $a$ is a constant related to the size, modulus and electronic mismatch of the solute with Al matrix and $\bar{C}$ is the average solute concentration in the matrix.

**Grain Size Effect**

The effect of grain refinement on the strengthening of aluminum alloys can be described by the Hall-Petch equation [Hall 1951, Petch 1953]:

$$\sigma_y = \sigma_i + kd^{-1/2}$$  \hspace{1cm} (2.6)

where $\sigma_y$ is the yield strength, $\sigma_i$ is the frictional stress of the lattice, $d$ is the average grain diameter and $k$ is constant for a given alloy system, characterizing the difficulty of transmitting slip across the grain boundary. Although $k$ is small in aluminum alloys the strengthening effect can be significant at very fine grain sizes. However, in 6000 series aluminum alloys there is little dependence of the strength on the grain size over the range which is commercially available at present (~27 to 46 μm) [Burger et al. 1995].

**Dislocation Hardening**
Cold forming operations can cause significant hardening in aluminum alloys due to the increase in dislocation density, \( \rho \). The contribution from dislocation hardening to the yield strength is given by [Mecking and Kocks 1981]:

\[
\sigma_d = \alpha M G b \rho^{1/2}
\]  

(2.7)

where \( \alpha \) is a constant approximately equal to 0.33, \( G \) is the shear modulus, \( M \) is the Taylor factor [Haasen 1986], and \( b \) is the magnitude of the Burgers vector.

2.6.1 Precipitation Hardening

The precipitation hardening theories have been reviewed in detail in the past decades [Brown and Ham 1971, Gerold 1979, Ardell 1985, Lloyd 1985]. The usual approach to treat the precipitation hardening phenomenon is to consider the particles as an array of point obstacles interacting with dislocations, Figure 2.5. When a gliding dislocation encounters an obstacle of the array, it bows out to some angle \( 0 \leq \varphi \leq \pi \). By increasing the applied stress the bowing angle becomes smaller until it reaches a critical value, \( \varphi_c \), when the obstacle is overcome and the dislocation moves forward. \( \varphi_c \) is considered as the (critical) breaking angle of the dislocation. An obstacle may be classified as weak or strong depending on whether the dislocation must bend through a large or a small \( \varphi_c \), in order to continue past the obstacle.

2.6.1.1 Obstacle Strength

The maximum interaction force between the obstacle and the dislocation, or alternatively defined, the obstacle strength, \( F \), can be determined by the force balance sketched in Figure 2.5:

\[
F = 2 \Gamma \cos \left( \frac{\varphi_c}{2} \right)
\]  

(2.8)
Figure 2.5 – Schematic presentation of the penetration of a random array of point obstacles by a dislocation [Ardell 1985].
where $\Gamma$ is the line tension of the dislocation ($F$ has been shown as $F_m$ in Figure 2.5). For a large breaking angle, i.e. a weak obstacle, $F$ is small and hence the obstacle is easily sheared by the dislocation (cutting mechanism). For a small $\varphi_c$, i.e. strong obstacle, on the other hand, $F$ is large and the obstacle imposes larger resistance to the dislocation motion before being overcome. When $\varphi_c = 0$, i.e. $F = 2\Gamma$, the obstacle is non-shearable and the dislocation bypasses the obstacle, leaving a dislocation loop around it (Orowan mechanism), Figure 2.6.

2.6.1.2 Contribution of Precipitation Strengthening to the Yield Strength

The critical stress, $\tau_c$, required for the dislocation to break free of the obstacle is related to the radius of curvature of the dislocation, $R_c$ [Brown and Ham 1971, Ardell 1985, Lloyd 1985, Embury et al. 1989]:

$$\tau_c = \frac{\Gamma}{bR_c}$$  \hspace{1cm} (2.9)

Also, from the geometry of Figure 2.5, $R_c$ is related to the effective obstacle spacing, $L$:

$$2R_c \sin \left(\frac{\varphi_c}{2}\right) = L$$  \hspace{1cm} (2.10)

where $\frac{\varphi_c}{2} = \frac{\pi}{2} - \frac{\varphi_c}{2}$. Using equation (2.8) and replacing for $R_c$ in equation (2.9):

$$\tau_c = \frac{F}{bL}$$  \hspace{1cm} (2.11)

Converting from $\tau_c$ to the tensile strength [Courtney 1990], equation (2.11) can be re-written for the contribution of precipitation strengthening to the yield strength, $\sigma_{ppt}$:

$$\sigma_{ppt} = \frac{MF}{bL}$$  \hspace{1cm} (2.12)

where $M$ is the Taylor factor (3.06 for FCC metals) [Haasen 1986].
Figure 2.6 – Schematic view in three sequences of the (a)–(c) Orowan mechanism, (d)–(f) cutting mechanism [Gerold 1979].
2.6.1.3 Obstacle Spacing

The effective obstacle spacing is dependent on the obstacle strength [Brown and Ham 1971, Gerold 1979, Ardell 1985, Lloyd 1985, Courtney 1990]. For weak obstacles the dislocation line is nearly straight and the mean obstacle spacing is large in comparison to the mean center-to-center distance between the particles. The effective obstacle spacing for these obstacles is derived based on the so-called Friedel statistics [Friedel 1962, Fleischer and Hibbard 1963, Fleischer 1964]. For a square lattice of \( N_s \) particles per unit area, the Friedel spacing is given by [Lloyd 1985, Ardell 1985]:

\[
L_F = \frac{L_s}{\left( \cos \frac{\phi_c}{2} \right)^{1/2}}
\]  

(2.13)

where \( L_s \) is the square lattice spacing, related to \( N_s \) by the following relationship:

\[
L_s = \frac{1}{N_s^{1/2}}
\]  

(2.14)

Using the Friedel spacing, \( \tau_c \) is derived as [Brown and Ham 1971, Lloyd 1985, Ardell 1985]:

\[
\tau_c = \frac{2\Gamma}{bL_s} \left[ \cos \left( \frac{\phi_c}{2} \right) \right]^{3/2}
\]  

(2.15)

For constant line tension where \( \Gamma = \frac{1}{2} Gb^2 \) (\( G \) is the shear modulus), equation (2.15) is written as:

\[
\tau_c = \frac{Gb}{L_s} \left[ \cos \left( \frac{\phi_c}{2} \right) \right]^{3/2}
\]  

(2.16)

The results of the computer simulations of dislocation glide in a two dimensional random array of point obstacles [Kocks 1966b, Forman and Makin 1966] have shown substantial agreement with equation (2.16) for weak obstacles where \( \phi_c \) is larger than 120° [Brown and Ham 25]
1971], as shown in Figure 2.7. For strong obstacles ($\phi_c \leq 100^\circ$), Brown and Ham [1971] have suggested the following relationship for $\tau_c$:

$$\tau_c = \frac{0.8Gb}{L_i} \cos \left( \frac{\phi_c}{2} \right)$$  \hspace{1cm} (2.17)

### 2.6.1.4 Superposition of Strengthening Effects

The precipitation hardening processes in aluminum alloys usually involve precipitates with a distribution of strengths. This may result from the coexistence of more than one type of precipitate in the microstructure and/or the size distribution of the precipitates. The most common expressions for the critical strength of two types of obstacles, including the results of the early computer experiments by Forman and Makin [1967], have been presented in the review articles by Brown and Ham [1971] and Ardell [1985]. Generally, a linear addition law is accepted for the mixture of a small number of strong obstacles with a large number of weak ones [Brown and Ham 1971, Ardell 1985]:

$$\tau = \tau_1 + \tau_2$$  \hspace{1cm} (2.18)

For all the other combinations of obstacle strengths and numbers, the so-called Pythagorean superposition law has shown close agreements with the results of computer experiments [Brown and Ham 1971, Ardell 1985]. The Pythagorean superposition law, which has originally proposed by Koppenaal and Kuhlmann-Wilsdorf [1964], is given by:

$$\tau^2 = \tau_1^2 + \tau_2^2$$  \hspace{1cm} (2.19)

It should be mentioned that for the superposition of the strengthening contributions from the matrix, including solid solution, and precipitates the linear addition law is the usual relationship [Ardell 1985].
Figure 2.7 – The critical stress as a function of $\phi$ ($\phi_e$ in the text). Solid curve: computed experimental results; dashed curve: critical stress calculated for square lattice of obstacles (see Brown and Ham [1971] for the equation); dashed-dotted curve, critical stress calculated according to the Friedel relationship (equation 2.15) [Brown and Ham 1971, original work: Foreman and Makin 1966].
Superposition of the strengthening effects of different obstacles has also been the subject of a recent computer experiment [Zhu et al. 1999]. Zhu et al. [1999] have proposed the following relationship for the superposition of the strengthening effects of two different types of precipitates in alloys:

$$\tau^\alpha = n_A^{\alpha/2} \tau_A^\alpha + n_B^{\alpha/2} \tau_B^\alpha$$

(2.20)

where $n_A$ and $n_B$ are the density fractions of particles $A$ and $B$ ($n_A + n_B = 1$) and $\alpha$ is a numerical exponent between 1 (linear addition law) and 2 (Pythagorean addition law).

### 2.6.1.5 Precipitation Hardening Mechanisms

The strengthening due to the precipitates in Al alloys is considered to arise from the following dislocation-particle interaction mechanisms [Brown and Ham 1971, Gerold 1979, Ardell 1985, Lloyd 1985, Embury et al. 1989]:

1. **Chemical strengthening** – associated with the creation of increased interfacial energy due to particle shearing.
2. **Stacking-fault strengthening** – due to the difference in stacking-fault energy between the particle and the matrix.
3. **Modulus strengthening** – due to the differences in the elastic moduli between the particles and the matrix.
4. **Coherency strengthening** – due to the elastic misfit of the particle in the matrix.
5. **Atomic order strengthening** – associated with the creation of an anti-phase boundary when a glide dislocation passes through an ordered precipitate.
6. **Orowan strengthening** – due to the dislocation looping around the non-shearable particles.
Embury et al. [1989] have tabulated the major theoretical formulations for these strengthening mechanisms, Table 2.1. Additional theoretical relationships from the literature, which are not included in Table 2.1, are summarized in Table 2.2.

2.7 Process Modeling

There has been an increasing interest in process modeling in aluminum alloys over the past decade [e.g., Shercliff and Ashby 1990a & 1990b, Grong and Myhr 1991, Ashby 1992, Shercliff et al. 1992]. The concept of process modeling for age hardening of aluminum alloys was first introduced by Shercliff and Ashby [1990]. A process model was defined as “a mathematical relation between the process variables (alloy composition, and the heat treatment temperature and time) and the alloy strength or hardness based on physical principles (thermodynamics, kinetic theory, dislocation mechanics and so on)”. Process modeling for aluminum alloys was further combined with the concept of internal state variables [Richmond 1986] to describe the microstructural evolution, expanding the modeling potentials to non-isothermal thermal processing [Ashby 1992, Shercliff et al. 1992]. Recently, Grong and Shercliff [2000] have presented a comprehensive review of the microstructural modeling in metal processing based on the internal state variable approach.

According to the internal state variable approach the material response of interest, \( P_t \), is defined in terms of the appropriate internal state (i.e. microstructural) variables, \( S_1, S_2, \ldots \):

\[
P_t = f_i(S_1, S_2, \ldots) \quad (2.21)
\]

The evolution of microstructure is then described in terms of differential variation of the internal state variables with time, considering that each state variable may be a function of other state variables as well as temperature:
Table 2.1 – The basic formulations for the particle-strengthening mechanisms. \( f \) and \( r \) are the volume fraction and radius of the (spherical) particles [Embury et al. 1989].

<table>
<thead>
<tr>
<th>Strengthening Mechanism</th>
<th>Formula</th>
<th>Symbols</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical-surface</td>
<td>( \tau_{cs} = \left( \frac{6\gamma_s^2 b}{\pi T} \right)^{1/2} \frac{1}{r} )</td>
<td>( \gamma_s = \text{surface energy} )</td>
<td>44</td>
</tr>
<tr>
<td>Stacking fault</td>
<td>( \tau_{\text{sf}} = \Delta \sigma \left( \frac{3\pi^2 f r}{32T b^2} \right)^{1/2} )</td>
<td>( \Delta \sigma = \text{difference in stacking-fault energy between matrix and particle} )</td>
<td>40</td>
</tr>
<tr>
<td>Modulus</td>
<td>( \tau_{G} = \frac{\Delta G}{4\pi^2} \left( \frac{f}{T} \right)^{1/2} \left[ 0.8 - 0.143 \ln \left( \frac{1}{f} \right) \right]^{1/2} )</td>
<td>( \Delta G = \text{difference in modulus between matrix and particle} )</td>
<td>45</td>
</tr>
<tr>
<td>Coherency</td>
<td>( \tau_{co} = k(eG)^{1/2} \left( \frac{f b}{T} \right)^{1/2} )</td>
<td>( e = \text{misfit parameter} )</td>
<td>46</td>
</tr>
<tr>
<td>Order</td>
<td>( \tau_0 = \frac{\sigma_{\text{APB}}}{2b} \left[ \left( \frac{4 \sigma_{\text{APB}} f}{\pi T} \right)^{1/2} - f \right] ) for ( r &lt; \frac{T}{\sigma_{\text{APB}}} )</td>
<td>( \sigma_{\text{APB}} = \text{antiphase-boundary energy} )</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>and</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \tau_0 = \frac{\sigma_{\text{APB}}}{2b} \left[ \left( \frac{4 f}{\pi} \right)^{1/2} - f \right] ) for ( r &gt; \frac{T}{\sigma_{\text{APB}}} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orowan</td>
<td>( \tau = \frac{0.8 Gb}{2\pi(1 - \nu)^{1/2} L} \ln \left( \frac{2r}{r_0} \right) )</td>
<td>( L = \text{clear interparticle spacing} )</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>( r_0 = \text{inner cut-off radius} \approx b )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2 – Additional formulations for the particle-strengthening mechanisms.

<table>
<thead>
<tr>
<th>Strengthening Mechanism</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coherency Strengthening</td>
<td>( \tau_{cs,\text{max}} = 1.84G\varepsilon f^{1/2} )</td>
<td>Ardell [1985]</td>
</tr>
<tr>
<td><strong>(maximum)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus Strengthening</td>
<td>( \tau_G = \frac{\Delta G}{4\pi} \left( \frac{f}{2} \right)^{1/2} )</td>
<td>Cartaud et al. [1976]; see also Gomiero et al. [1992] and Starink et al. [1999].</td>
</tr>
<tr>
<td>Order</td>
<td>( \tau_{O,\text{max}} = 0.81 \gamma_{\text{apb}} \left( \frac{3\pi f}{8} \right)^{1/2} )</td>
<td>Ardell [1985]; see also Huang and Ardell [1988], Lee and Park [1998], and Starink et al. [1999].</td>
</tr>
</tbody>
</table>
\[ \frac{dS_1}{dt} = g_1(T, S_1, S_2, ...) \] (2.22)

\[ \frac{dS_2}{dt} = g_1(T, S_1, S_2, ...) \] (2.23)

Depending on the problem, the microstructural evolution can often be described by one or two variables [Grong and Shercliff 2000]. The microstructure of an age hardening aluminum alloy may be described by the evolution of two state variables, e.g. the volume fraction, \( f \), and the number density, \( N_v \), or the particle radius, \( r \) [Shercliff et al. 1992]. The theoretical relationships for precipitation hardening due to the different strengthening mechanisms, Tables 2.1 and 2.2, suggest that \( f \) and \( r \) are the most relevant variables in modeling of the yield strength. Solution of the above differential equations generally requires stepwise integration in time [Grong and Shercliff 2000]. Upon determination of the state variables, they are substituted in the response equation to obtain the material response of interest. For isothermal models the state variables may be directly formulated in integrated forms [Shercliff et al. 1992].

Parallel with the increased knowledge on the microstructural evolution and their corresponding relationships to the properties in Al alloys, the process models have continuously incorporated more complexities of the precipitation processes [e.g. Gomiero et al. 1992, Deschamps and Brechet 1999, Starink et al. 1999b, Poole et al. 2000, Myhr et al. 2001]. The contribution of individual strengthening mechanisms to the yield strength is considered for an Al-Li alloy [Gomiero et al. 1992] as well as Al-Li-Cu-Mg alloys [Starink et al 1999b]. The evolution of the precipitate strength during aging and the effect of precipitate size distribution is incorporated in the models developed for an Al-Zn-Mg alloy [Deschamps and Brechet 1999], AA7030 and AA7108 [Poole et al. 2000] and Al-Mg-Si alloys [Myhr et al. 2001]. The formulation of these later models enforces the transition from shearable to non-shearable obstacles to correspond to the peak strength. Deschamps and Brechet [1999] and Myhr et al.
[2001] have applied the Friedel formulation for yield strength for the entire aging period (i.e. both cutting and Orowan mechanisms). Poole et al. [2000], on the other hand, have chosen the relationship proposed by Forman and Makin [1966] for estimation of the strengthening due to precipitates. A process model for Al-Mg-Si alloys has also been developed by Vasiliev et al. [1997]. The model uses the Friedel formulation and assumes a constant strength for the obstacles. The peak strength is considered to coincide with the start of the coarsening process and not necessarily with the shearable to non-shearable transition [Vasiliev et al. 1997].

A process model incorporating dissolution reactions has been developed by Myhr and Grong [1991a & 1991b] for 6082-T6 aluminum alloys at elevated temperatures. The model has been applied for prediction of strength losses in the heat-affected zone of 6082-T6 involving the dissolution of $\beta''$ precipitates.
CHAPTER 3

SCOPE AND OBJECTIVES

The present work aims at obtaining a comprehensive knowledge on the precipitation hardening behaviour of AA6111 through experimental investigation as well as fundamentally based process model development for the following thermal histories:

- artificial aging of the solution treated, as-quenched, materials,
- artificial aging of the materials with variable levels of natural aging.

The yield strength predictions for the entire aging process including underage, peak-age and overage conditions are sought. This goal is achieved through:

- thoroughly investigating the effect of the thermal histories of interest on the evolution of microstructure and properties of the alloy,
- combining the acquired knowledge with established physical theories and models, through which the behaviour of the material can be well described,
- developing the process model as well as the related microstructural sub-models,
- calibrating the process model using the experimental results,
- validating the model and the related microstructural sub-models with independent laboratory experiments.

The model will be the first process model developed for AA6111. The process model along with the acquired knowledge will make significant contributions to the field of process modeling in aluminum alloys as well as the fundamental understanding of processing-structure-relationships in AA6111.
CHAPTER 4

EXPERIMENTAL METHODOLOGY

4.1 Introduction

In this chapter, the material, the heat treatment procedures and the experimental methods used for this investigation will be described.

4.2 Material

The AA6111 alloy used in this study was supplied by Alcan International in the form of ~1 mm thick sheets which had been cold rolled and then solution treated on a commercial continuous annealing line. The chemical composition of the alloy is given in Table 4.1. Figure 4.1 shows the microstructure of the as-received T4 material. The optical micrograph is the cross sectional view of the sheet material, obtained after the usual polishing procedure and etching for 20 minutes in a solution of 5g NaOH in 100 ml of water.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA6111</td>
<td>0.79</td>
<td>0.60</td>
<td>0.70</td>
<td>0.25</td>
<td>0.20</td>
<td>0.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

4.3 Thermal Processing

The thermal processing of all samples was started by a solution heat treatment at 560°C (±2°C) for 10 minutes in a salt bath, unless the starting material had to be in the as-received T4
Figure 4.1 – The optical micrograph for the as-received AA6111-T4 sheet (cross sectional view). The black spots are mainly artifacts from sample preparation (samples were polished and etched for 20 minutes in a solution of 5g NaOH in 100 ml of water).
condition. This combination of time and temperature was chosen to restore the maximum solid solution before quenching and subsequent aging processes. Following the solution treatment the samples were taken out of the salt bath and quenched (quench rate ~ 170°C/s) in tap water at room temperature (~ 20°C). Two different thermal treatments were followed immediately after water quench:

a) Direct aging at 20-250°C (single-step)

The samples (for tensile, hardness, electrical resistivity, TEM and DSC tests) were up-quenched to the aging temperature in the range of 60-250°C by transferring them into an oil bath (60-180±1°C) or a salt bath (200-250±3°C), where they were kept for the desired time. The samples were then water quenched to room temperature. For long aging processes the samples were transferred to an air furnace after initial aging in the oil or salt bath. The aging medium for the isothermal calorimetry samples was air. Figure 4.2(a) shows a schematic presentation of these direct aging processes. A number of TEM samples were ramp heated (10°C/min) immediately after quenching from the solution treatment temperature, Figure 4.2(b). For the cases of aging at 20°C, the samples were kept at the room temperature after solution treatment and the subsequent quenching, Figure 4.2(c).

b) Natural aging followed by artificial aging (two-step)

The samples (for tensile, hardness, electrical resistivity, TEM and DSC tests) were first kept at room temperature for the desired period (in the range of 24 hour – 2 years), then aged at 180°C in an oil bath. The samples were then water quenched to room temperature. As in the previous case, for long aging periods, the samples were aged in an air furnace after aging initially in the oil bath. The schematic presentation of this thermal history is shown in Figure 4.3(a). In those experiments, where the behaviour of the as-received T4 material during artificial aging was under investigation, the T4 samples were artificially aged for the desired time at temperature. As
Figure 4.2 – Schematic presentation of direct aging treatments: (a) isothermal artificial aging, (b) ramp heating to the desired temperatures, (c) aging at room temperature.
Figure 4.3 – Schematic presentation of two step aging treatments: (a) aging at room temperature followed by isothermal artificial aging, (b) isothermal artificial aging of T4 samples, (c) ramp heating of T4 sample to the desired temperature.
in the previous cases, aging at 180°C was conducted in an oil bath, followed by aging in an air furnace (180±2°C) for long processes. A salt bath was used for aging at 200°C and 220°C. The isothermal calorimetry experiments on the T4 samples were run in air at the temperature range of 180-220°C. These heat treatment processes are schematically shown in Figure 4.3(b). A T4 sample, used for TEM studies, was also ramp heated at a rate of 10°C/min to 275°C, Figure 4.3(c).

4.4 Experimental Procedure

The experimental procedures are categorized according the testing methods used.

4.4.1 Tensile and Hardness Tests

The mechanical behavior of the material as a function of thermal history was studied by tensile and hardness tests. Tensile tests were conducted at room temperature using a modified MTS servo-hydraulic system with an INSTRON 8500 controller at a displacement rate of 5 mm/min which corresponded to a nominal strain rate of 2×10⁻³ s⁻¹. An INSTRON extensometer with a gauge length of 40 mm was used to measure displacement in the reduced section of the tensile samples. The recorded data for load, \( F_i \), and displacement, \( \Delta l \), were converted to engineering stress and engineering strain and then to the true stress and true strain according to the following relationships:

\[
S = \frac{F_i}{A_o} \quad (4.1)
\]

\[
e = \frac{\Delta l}{l_o} \quad (4.2)
\]

\[
\sigma = S(1 + e) \quad (4.3)
\]

\[
\varepsilon = \ln(1 + e) \quad (4.4)
\]

39
where $S$, $e$, $\sigma$, $\epsilon$, $l_0$ and $A_0$ are the engineering stress, engineering strain, true stress, true strain, initial length and initial area, respectively. The yield strength was determined using the 0.2% offset method. The repeats of tensile tests showed that the yield stress measurement error was in the range of ± 5 MPa. Figure 4.4 shows the schematic drawing of the tensile sample. The samples were cut in the rolling direction.

The hardness tests were performed using a MICROMET 3 Vickers Microhardness Tester using a load of 1 kgf. The average value of five readings was used for each data point.

### 4.4.2 Electrical Resistivity

The electrical resistance measurements were performed by a four-point probe method, using a rig designed and made in our laboratory. Figure 4.5 shows the schematic of the electrical system. The applied current was reversed (30 HZ) in order to eliminate uncertainty in measuring the voltage drop across the sample due to drift of the zero point. The current amplitude was kept low (10-20 mA) to inhibit the sample heating during the measurement period. The potential drop data, recorded by the data acquisition system, were converted to the resistance data by the program written for this special purpose using the LABVIEW software. The resistance, $R$, readings were used to calculate the resistivity, $\rho$, values as:

$$\rho = \frac{RA}{l} \quad (4.5)$$

where $A$ is the cross sectional area of the sample and $l$ is constant distance between the two potential probes (54 mm). Acquiring a large population of resistance data (~ 20,000) minimized the error due to the electrical system.
Figure 4.4 – Schematic drawing of the tensile sample (thickness = 1 mm).

Figure 4.5 – Schematic presentation of the resistivity measurement rig.
In order to confirm the validity of the measured data and to determine the percentage error, an exhaustive calibration procedure was carried out on different materials with varied dimensions at different test temperatures. The readings on AA1100, commercially pure Al, and AA7475 alloy were compared to the corresponding data obtained from conductivity measurements using eddy current tests. In each case a systematic positive error of approximately 3% was detected. Based on the calibration data, the samples were chosen to be in the form of strips with the dimensions of 100 mm in length, 10 mm in width and 1 mm in thickness. The reproducibility of the data was examined by repeating the measurements on the as-quenched and T4-AA6111 samples at 77 K, 273 K and 293 K (i.e. room temperature). For 273 K and 77 K tests, the probe was attached to the sample and immersed into ice water or liquid nitrogen, respectively. Being very sensitive to the temperature changes, the room temperature data showed a large scatter. For 77 K measurements, the maximum error encountered choosing different samples was approximately 3%, whereas the maximum error for a single sample was about 0.4%. In order to maintain a constant temperature throughout the measurements and minimize thermal contribution to electron scattering, measurements at 77 K were chosen for the subsequent electrical resistivity studies.

4.4.3 Isothermal Calorimetry

Isothermal calorimetry experiments were conducted by SETARAM Inc. in Caluire, France using a C 80 Calorimeter, at a temperature range of 160-220°C. Two sets of samples were tested. The first set were solution treated (10 min at 560°C), water quenched and then immediately transferred to the calorimeter vessel at the set temperature (hold time was less than 3 minutes). For the second set of samples no heat treatments were performed on the as-received T4 samples prior to the isothermal calorimetry experiments. Samples were cut in pieces of 10
mm x 10 mm x 1 mm. For each test, four pieces were dropped (gravity) in the vessel, simultaneously.

Two tests were run for each sample at the desired temperature. The heat evolution in the first run included the initial endothermic effect due to the introduction of the sample to the calorimeter vessel and its heating to the set temperature as well as the heat effects due to the precipitation and dissolution reactions. The first test was carried out up until the heat flow reduced to a very low level (i.e. \(1-4\times10^{-5}\) W/g). The sample was then removed and cooled down to room temperature and then tested for the second run. Having reached a zero heat effect (approximately) in the first run, the second test showed only the initial endothermic effect due to the heating of the sample to the set temperature. The final corrected thermogram was then obtained by subtracting the heat effect result of the second test from the corresponding heat effect of the first test. Figure 4.6 illustrates the heat flow due to the first run, i.e. curve “I”, second run, i.e. curve “II”, as well as the final, i.e. Resultant, thermogram. The introduction of the sample to the calorimetry vessel, running at the set temperature, caused initial instability in the calorimeter. The duration of this initial instability was approximately 7-10 minutes, during which no heat effect change was recorded.

4.4.4 Differential Scanning Calorimetry (DSC)

DSC tests were conducted at Alcan International’s Kingston Research and Development Centre using a TA Instruments Model 2910 calorimeter. The reference material was super purity aluminum with the same mass as the test sample. A heating rate of 10°C/min and argon atmosphere were used for all measurements. The heat released or absorbed, corresponding to a precipitation or a dissolution reaction, respectively, was recorded as a function of temperature. The corrected final trace was obtained by subtracting the baseline obtained from a super purity
Figure 4.6 – The heat effects recorded in the first and second runs of the isothermal calorimetry experiment. The corrected trace, i.e. Resultant, is obtained by subtracting trace II from trace I.
Al-Al run from the heat effect data recorded for the test sample. The DSC run on the as-quenched sample was performed immediately after solution treatment (10 min at 560°C, water quenched). All other DSC experiments were conducted on pre-heat treated samples sent from UBC. In the case of the samples naturally aged for two weeks before the DSC runs, pre-arrangements were made to assure the exact natural aging duration. The samples were approximately 3 mm in diameter by 1 mm in thickness. The exothermic reactions were plotted upward and endothermic reaction downward on the DSC thermograms (see e.g. Figure 5.12).

4.4.5 Transmission Electron Microscopy (TEM)

TEM observations were performed by Drs. A. Perovic and X. Wang in the Brockhouse Institute of Materials Research at McMaster University using a conventional Philips CM-12 electron microscope operating at 120kV. The heat treatments on TEM samples were conducted at UBC. TEM thin foils were prepared either at McMaster University or at Alcan International’s Kingston Research and Development Centre. Quantitative TEM analysis was conducted on 4 to 10 fields of observation (i.e. 90 to 400 precipitates counted or measured for size) for each thermal history. Assuming that the precipitate distribution was isotropic, the number of precipitates for each field of observation was calculated by multiplying the counted end-on precipitates by three. The thickness of the foil was measured by counting the number of extinction fringes at an inclined grain boundary [Williams and Carter 1996]. The number density for each field was calculated by dividing the number of precipitates by the volume (i.e. foil thickness x area) of the field. Precipitate size measurements were conducted using Image Tool software. The volume fraction of precipitates for each data point (i.e. thermal history) was estimated roughly by multiplying the average number density by the average volume per precipitate (the effect of size distribution was not taken into account for this approximate estimation).
CHAPTER 5

EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Results

5.1.1 Precipitation Hardening Behaviour of the Solution Treated Material

The experimental results are categorized according to the experimental methods of investigation. Special attention is given to the behaviour of the material during aging at 180°C and 20°C.

5.1.1.1 Yield Strength

The age hardening response of the solution treated material after aging in the temperature range of 20-250°C was examined using room temperature tensile testing. Figure 5.1 shows the evolution of the yield strength during aging at this temperature range. The yield strength of the as-quenched sample, representing the supersaturated solid solution condition, is ~ 60 MPa. The strength then increases rapidly during aging at high temperatures. In contrast, the kinetics of age hardening at low temperatures is slow. It is also observed that the peak strength values for the temperature range of 140-220°C are similar. The aging curve for 250°C, on the other hand, shows that the peak strength is significantly smaller than those at the temperature range of 140-220°C.

Aging at 180°C

A closer examination of the aging curve at 180°C, Figure 5.1, shows that the yield strength increases rapidly from 60 MPa for the as-quenched sample to 290 MPa and 310 MPa.
Figure 5.1 – The evolution of the yield strength of the solution treated samples during aging in the temperature range of 20-250°C.
after 30 minutes and 1 hour of aging, respectively. The yield strength further increases at a much slower rate to the peak value of 340 MPa after 7 hours of aging. Thus, approximately 80% and 90% of the maximum increase in the yield strength occurs in the first 30 minutes and 1 hour of aging at 180°C, respectively. The yield strength decreases very slowly by aging beyond the peak, dropping only to 335 and 330 MPa after 24 and 90 hours of aging, respectively.

**Aging at 20°C (Natural Aging)**

The evolution of yield strength during aging at 20°C has also been shown in Figure 5.1. The change in the yield strength during the first hour of aging at room temperature is very small. Further aging at room temperature, however, results in a substantial increase in the yield strength. The yield strength increases relatively rapidly to 110 MPa after 24 hours of natural aging, followed by slower increase to 150 MPa and 170 MPa after 2 weeks and 2 years of natural aging, respectively. The evolution of yield strength during natural aging can be approximated by a logarithmic relationship as shown in Figure 5.2:

$$\sigma_y = 12.3 \ln(t) + 67$$  \hspace{1cm} (5.1)

where $t$ is in hour and $\sigma_y$ is in MPa. Equation (5.1) is valid for the natural aging time range of 1 hour to 2 years.

**5.1.1.2 Electrical Resistivity**

Figure 5.3 shows the variation in electrical resistivity as a function of time at different temperatures. It is observed that the value of resistivity increases initially, reaches a maximum or a plateau, and then for temperatures above 90°C decreases with aging time. The magnitude of the resistivity increase is temperature dependent, i.e. it is larger for lower temperatures. In
Figure 5.2 – The evolution of yield strength during natural aging.

\[ \sigma_y = 12.3 \ln(t) + 67 \text{ MPa} \]

Figure 5.3 – The evolution of electrical resistivity during aging in the temperature range of 20-200°C.
addition, closer examination of the increasing part of the curves (see for example Figures 5.4) indicates that the resistivity initially changes at a high rate and then after a characteristic time the rate of change decreases dramatically. It can be observed that the transition occurs over a range of time rather than at a definite point. In this work, the point of deviation from the initial linear increase in resistivity is defined as the transition time, \( t_{tr} \). The rate of the increase in resistivity for \( t \leq t_{tr} \) can then be represented by \( \frac{1}{t^{\prime}_{tr}} \). Figure 5.5 shows that the variation of \( \frac{1}{t^{\prime}_{tr}} \) with aging temperature follows an Arrhenius-type relationship:

\[
\frac{1}{t^{\prime}_{tr}} = \frac{1}{t^{\prime}_{tr}^0} \exp\left(-\frac{Q}{RT}\right)
\]

where, \( t^{\prime}_{tr}^0 \) is the pre-exponential constant, \( Q \) is the activation energy for the atomic process that causes the increase in the electrical resistivity for \( t \leq t_{tr} \), \( R \) is the universal gas constant and \( T \) is the absolute temperature. The data for the Arrhenius plot of Figure 5.5 include the temperature range of 20-120°C (higher aging temperatures are not included, because of the very short aging times for the transition). The activation energy is found to be 38 ± 5 kJ/mole (~ 0.40 ± 0.05 eV). It should be noted that alternative definitions for the transition point in the transition time range do not significantly change the measured activation energy.

**Aging at 180°C**

The change in the electrical resistivity during aging at 180°C has been shown in Figure 5.3. It is observed that the resistivity initially rises to a maximum after 5 minutes of aging. It then decreases by further aging to levels significantly lower than the resistivity of the as-quenched material. The change in the rate of decrease in resistivity with aging time can also be examined by plotting the resistivity data with a linear time scale, as shown in Figure 5.6. It is
Figure 5.4 – The transition from a rapid to a slow increase in resistivity is shown for aging at (a) 20°C and (b) 60°C.
Figure 5.5 – The Arrhenius-type plot for $\frac{1}{t_w}$. 

$Q = 38$ kJ/mole
Figure 5.6 – The evolution of electrical resistivity during aging at 180°C. (a) and (b) have different time scales.
clear that the decrease in resistivity is initially very rapid, but the rate reduces drastically after 4 hours of aging. This aging time corresponds to the approximate time to reach the peak strength.

**Aging at 20°C**

The evolution of the electrical resistivity during natural aging has also been shown in Figure 5.3. A significant increase in resistivity is observed during natural aging up to 30 days. It has also been shown that the resistivity increases by a faster rate during the first few hours of natural aging, Figure 5.4(a). The change in the resistivity during 30 to 160 days of natural aging (the longest time measured) is insignificant.

**5.1.1.3 Isothermal Calorimetry**

The kinetics of precipitation during aging at the temperature range of 160-220°C has been studied by isothermal calorimetry. Figure 5.7(a) shows the thermograms at various temperatures. As, discussed in section 4.4.3, the calorimeter does not record the heat evolution data during the first 7-10 minutes of aging, i.e. $t_0$, when it is disturbed by the introduction of the sample. Following the stabilization of the calorimeter at time $t_0$, an exothermic heat effect, representing precipitation reactions, is recorded. The rate of heat release, $\frac{dQ}{dt}$, increases rapidly to a maximum at time $t^*$ and then decays to zero when the reaction reaches completion or the heat generation becomes too small for measurement. The thermograms for aging at 180°C, 200°C and 220°C show sharp maxima (particularly for the cases of aging at 180°C and 220°C) and the periods $\Delta t = t^* - t_0$ are very short. The trace for the case of aging at 160°C, however, does not show sharp maximum point and the corresponding $\Delta t$ is longer. The time to reach the approximate zero heat evolution is designated as $t_f$. The characteristics times, $t^*$, $t_0$ and $t_f$ are
Figure 5.7 – (a) The isothermal calorimetry traces for aging at 160-220°C. (b) The characteristic times of the calorimetry experiments.
shown on the isothermal trace for aging at 180°C in Figure 5.7(b). The values obtained for \( \Delta t \) and \( t_f \), for different temperatures, are listed in Table 5.1. A comparison of the heat evolution with the yield strength evolution for aging at 180°C is shown in Figure 5.8. This shows that \( t_f \) is approximately equivalent to the time to reach the peak strength.

As each point on the thermogram represents the rate of heat release, the area under the trace represents the approximate total heat effect due to the precipitation reactions:

\[
total \ heat = \int_0^t \frac{dQ}{dt} \, dt
\]  

(5.3)

where the zero time has been shifted to \( t_0 \) (this will also be shown in detail in section 6.2.1.3). It is interesting to know that the total heat evolutions are very similar for all four cases of aging at 160°C, 180°C, 200°C and 220°C (see Table 5.1). The fraction of the heat evolved at a certain aging time, \( t \), is estimated by dividing the area under the curve up to the time \( t \) by the total area under the curve. The fraction of heat evolved at any aging time \( t \) represents the fraction of the precipitation reactions completed during that period of time, i.e. the relative volume fraction of precipitates, \( f_r \) (assuming that the reactions are complete for \( t = t_f \)):

\[
f_r = \frac{\int_0^t \frac{dQ}{dt} \, dt}{\int_0^{t_f} \frac{dQ}{dt} \, dt}
\]  

(5.4)

Figure 5.9 shows the evolution of the relative volume fraction during aging for the above aging temperatures. For the case of aging at 180°C, it is observed that the relative volume fraction of precipitates is approximately 30% and 90% after 5 minutes and 1 hour of aging, respectively. The relative volume fraction then rises to 100% after approximately 4 hours of aging at 180°C. Also, an interesting feature in this figure is the case of aging at 220°C, which
Table 5.1 – The characteristic times and the total heat evolved during the isothermal calorimetry of solution treated and T4 samples aged at various temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging Temperature (°C)</th>
<th>( \Delta t ) (s)</th>
<th>( t_f ) (hr)</th>
<th>Total Heat (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution Treated</td>
<td>160</td>
<td>410</td>
<td>12</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>24</td>
<td>4</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>64</td>
<td>2</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>32</td>
<td>1.7</td>
<td>10.4</td>
</tr>
<tr>
<td>T4</td>
<td>180</td>
<td>-</td>
<td>10</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>-</td>
<td>6</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>-</td>
<td>2</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Figure 5.8 – The heat evolution and yield strength during isothermal aging at 180°C. The zero time for isothermal calorimetry trace has been shifted to $t_0$. 
Figure 5.9 – The relative volume fraction of precipitates as a function of aging time.
shows a slightly different trend in the kinetics of transformation after 90% of transformation is completed.

Figure 5.10 compares the trends in the evolution of $f_r$ and yield strength for aging at 180°C and 220°C. It clearly shows that the relative volume fraction approaches unity when the yield strength reaches peak-age condition in the case of aging at 180°C. Although not shown here, this is also the case for aging at 200°C. Interestingly, in the case of aging at 220°C (Figure 5.10b), the peak strength is reached before the relative volume fraction of precipitates reaches unity ($f_r \approx 95\%$ at the peak-age).

### 5.1.1.4 Differential Scanning Calorimetry

In order to study the changes in the precipitation state during aging, a series of DSC runs have been conducted on the as-quenched material (solution treated) and the samples aged for various times at 180°C after solution treatment. The DSC thermograms for the as-quenched sample and the samples aged up to 7 hours at 180°C are shown in Figure 5.11. Following the information given in the literature (section 2.3.2), the exothermic peaks are designated as clusters, spherical GP zones (SGPZ), $\beta''$ and $Q'$ as shown in Figure 5.11. Also, comparing the temperature range of peak II (centered at $\sim 340^\circ$C) on the DSC trace for the as-quenched sample with the results of Miao and Laughlin [2000a] on AA6022 (see Figure 2.2), this peak is designated as $Q$. No designation for the small peak I (centered at $\sim 315^\circ$C) has been chosen at present, however, occurring between $Q'$ and $Q$ and consistent with the observations by Cayron and Buffat [2000], it is suggested to be related to the Q phase transitions. The important findings from the DSC traces are listed below:
Figure 5.10 – The evolution of the relative volume fraction of precipitates and yield strength during aging at (a) 180°C and (b) 220°C.
Figure 5.11 – The DSC thermograms for the as-quenched sample and the samples with various levels of aging at 180°C.
1. The peak associated with the cluster formation is present only on the DSC trace for the as-quenched sample.

2. Exothermic peak associated with SGPZ is present on the DSC traces for the as-quenched sample as well as the samples aged for 5 and 15 minutes at 180°C. The height of this peak apparently does not change during the first five minutes of aging, however, it decreases considerably by aging for 15 minutes. It finally starts to disappear after 30 minutes of aging at 180°C.

3. The exothermic peak associated with $\beta''$, which is the most prominent peak on the trace for the as-quenched sample, significantly decreases in magnitude after 30 minutes of aging. A very small heat effect for $\beta''$, overlapped by the peak associated with $Q'$, is observed on the DSC trace of the sample aged for 1 hour at 180°C.

4. The height of the $Q'$ peak decreases continuously during aging at 180°C aging, although this decrease is considerably smaller than that of the $\beta''$ peak.

5. Both SGPZ and $\beta''$ peaks are absent on the DSC trace of the sample aged for 7 hours at 180°C.

6. Peak I and II, associated with a precursor of $Q$ and the equilibrium $Q$, respectively, are invariable for all aging conditions up to 7 hours at 180°C.

7. An endothermic heat effect, i.e. trough A, is present on the DSC traces of the samples aged for 30 minutes and longer at 180°C. The depth of trough A increases significantly for the sample aged for 7 hours at 180°C.

   The DSC traces for the samples overaged for 24 and 120 hours at 180°C are shown in Figure 5.12. The following results are observed:
Figure 5.12 – The DSC thermograms for samples with various levels of overaging at 180°C.

The thermogram for the as-quenched sample is also illustrated for comparison.
1. The peaks associated with clusters, SGPZ and $\beta''$ are not present on the traces of the samples aged for 24 and 120 hours.

2. Q' peak is present for both cases of overaging. It is clear that the height of Q' peak (estimated from the zero heat evolution level) considerably reduces after aging for 24 hours at 180°C. In the case of the sample aged for 120 hours, the height of this peak is further reduced (negative compared to the line of zero heat evolution); resulting in a wide compound peak associated with both Q' peak and peak I. The peak associated with equilibrium Q has similar magnitudes in both cases of 24 and 120 hours of aging.

3. Trough A, which is present in both cases, becomes considerably wider and shifts to higher temperatures in the case of 120 hours of aging.

4. An exothermic peak, i.e. peak III centered at \( \sim 500^\circ C \), is present within the dissolution trough for Q. It should also be mentioned that this peak is present on the DSC traces for all aging conditions in this alloy. In agreement with the Thermo-Calc predictions for 6111 [Gupta et al. 1996] and AA6022 [Miao and Laughlin 2000a], this peak may be attributed to equilibrium $\beta$ ($\text{Mg}_2\text{Si}$).

It is interesting to compare the DSC traces for the above overaging conditions with that of a sample overaged for 6 months at 180°C. Although the starting material in the later case has been in the naturally aged condition, i.e. T4, the precipitation state should not be significantly different from that of a solution treated material overaged for that long period. It is clearly seen that the total heat effect is negative. Also, the peak associated with Q' and peak I are replaced by a wide trough. A small heat effect associated with Q peak as well as peak the peak attributed to $\beta$ are present in this case.
**Estimation of the Relative Volume Fraction from DSC results**

The evolution of the relative volume fraction of the precipitates during aging at 180°C can also be estimated using the DSC traces shown in Figure 5.11. Since the DSC peaks have overlaps and in some cases the height of a peak is the net effect of simultaneous exothermic and endothermic events, the volume fraction of the individual precipitates may not be obtained from the DSC traces. The following method is thus introduced to estimate the evolution of the relative volume fraction of the sum of all precipitates:

1. Zero heat evolution line is assumed to be the reference line for the evaluation of the exothermic and endothermic heat effects.

2. The net area under a DSC trace, as shown in Figure 5.13(a) for the solution treated sample, is taken as a measure for the total heat evolution due to precipitation. As an example, the area under the trace for the solution treated sample, i.e. SSS, is obtained as follows:

   \[ Area_{SSS} = \int_{T_1}^{T_2} \frac{dQ}{dt} dT \]  

   Although the integration of the heat flow over the temperature axis does not give the total heat evolved, it can be used as a measure for the heat effect for the relative volume fraction calculations.

3. The lower and upper temperature limits, \( T_1 \) and \( T_2 \), in equation (5.5) are chosen to be 60°C and 330°C, respectively. Choosing the initial temperature at 60°C eliminates the initial heat instability effects. Also, since only the first four exothermic peaks change during aging at 180°C up to the peak-age condition, the total area associated with the DSC traces up to the end of \( Q' \) peak is required for the volume fraction estimations for aging at 180°C. Due to the possible overlaps between \( Q' \) peak and peak I, \( T_2 \) is chosen up to the end of peak I, i.e. 330°C.
Figure 5.13 – (a) The area under DSC trace for the solution treated sample. (b) The relative volume fraction of precipitates formed during aging at 180°C.
4. The relative volume fraction of the precipitates formed during aging at 180°C is calculated as:

$$f_r = \frac{\int_{t_1}^{t_2} \frac{dQ}{dT} \, dt \bigg|_{SSS} - \int_{t_1}^{t_2} \frac{dQ}{dT} \, dt \bigg|_{t}}{\int_{t_1}^{t_2} \frac{dQ}{dT} \, dt \bigg|_{SSS} - \int_{t_1}^{t_2} \frac{dQ}{dT} \, dt \bigg|_{peak}} = \frac{Area_{SSS} - Area_{t}}{Area_{SSS} - Area_{peak}}$$

(5.6)

$Area_{t}$ and $Area_{peak}$ are the net areas (the sum of negative and positive areas) under the DSC traces for the samples aged for time $t$ and $t_{peak}$, respectively, where $t_{peak}$ is the time to reach the peak-age condition. Hence, $f_r$ estimated by equation (5.6), gives the relative volume fraction of precipitates based on the assumption that the precipitation reactions are complete for the peak-age condition. It should be mentioned that the net area for the aging time between 4 to 7 hours at 180°C, i.e. the peak-age condition, is very close to zero.

The results of the relative volume fraction estimation from the DSC results are compared with the relative volume fraction estimated from isothermal calorimetry in Figure 5.13(b). It is shown that the values estimated from DSC are in excellent agreement with the corresponding values from isothermal calorimetry. This method provides a simple procedure for estimation of the relative volume fraction from DSC traces. It can be especially useful for estimation of the relative volume fraction for low temperature aging processes, where the use of isothermal calorimetry equipment for very long aging times is not feasible and/or the sensitivity of the calorimeter is not high enough to record very small heat releases.

### 5.1.1.5 TEM Studies

The microstructural evolution of the alloy has been studied by transmission electron microscopy (TEM) in collaboration with the researchers in Brockhouse Institute for Materials Research, McMaster University.
**Combined DSC-TEM**

In order to confirm the precipitation state corresponding to the DSC peaks designated as \( \beta'' \) and \( Q' \), TEM observations have been made on the samples heated with the same rate as the DSC samples (i.e. 10\(^\circ\)C/min) after solution treatment. The samples have been heated to either 260\(^\circ\)C or 300\(^\circ\)C, i.e. the end temperatures for the DSC peaks \( \beta'' \) and \( Q' \), respectively. The results are shown in Figure 5.14. Two types of precipitates, needle-shape \( \beta'' \) and lath-shape \( Q' \), aligned parallel to \(<100>_{AI}\) are observed in the case of the sample ramped to 260\(^\circ\)C, Figure 5.14(a). \( \beta'' \) precipitates are identified by their round cross sections (i.e. end-on views). \( Q' \) precipitates, on the other hand, are recognized by their rectangular end-on cross sections and long face-on views (i.e. cross sections parallel to their long axes). Although both \( \beta'' \) and \( Q' \) precipitates are present for this heating condition, the number density of \( Q' \) appears to be significantly smaller than that of \( \beta'' \). In the case of the sample heated to 300\(^\circ\)C, the microstructure consists mainly of large \( Q' \) precipitate, Figure 5.14(b).

**Evolution of Microstructure during Aging at 180°**

Quantitative TEM analysis has been conducted on samples that have been solution treated and aged for various times at 180\(^\circ\)C. Figure 5.15 shows the TEM micrographs for the samples aged for 30 minutes, 1 hour and 7 hours at 180\(^\circ\)C. Two types of precipitates, needle-shape and lath-shape, aligned along \(<100>_{AI}\), are observed. The needle-shape precipitates are identified by their circular end-on views and the strain contrast around them when viewed face-on (readily noticeable in Figure 5.15c). The lath-shape precipitates, on the other hand, are recognized by their rectangular end-on and long face-on views. The results of the quantitative analysis of the microstructures are listed in Table 5.2. The main features are summarized as follows:
Figure 5.14 – [001]A1 bright field TEM micrographs for the solution treated samples ramp heated (10°C/min) to (a) 260°C and (b) 300°C. TEM observations by A. Perovic.
Figure 5.15 – [001]_{Al} bright field TEM micrographs for the solution treated samples aged for (a) 30 minutes at 180°C (the face-on views of the lath-shape precipitates are not visible in this micrograph), (b) 1 hr at 180°C and (c) 7 hours at 180°C. TEM observations by X. Wang.
Table 5.2 – The results of the quantitative TEM studies on the solution treated and naturally aged samples after aging for various times at 180°C. The quantitative TEM analysis has been conducted by X. Wang.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time at 180°C</th>
<th>Cross-sectional Area (nm²)</th>
<th>Length (nm)</th>
<th>No. Density ×10⁻²³ (m⁻³)</th>
<th>Volume Fraction</th>
<th>( \frac{N_{\text{needle}}}{N_{\text{lath}}} )</th>
<th>( \frac{f_{\text{needle}}}{f_{\text{lath}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution treated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.58</td>
<td>4.58</td>
<td>4.16</td>
<td>0.013</td>
<td>1.092</td>
<td>2.0×10⁻³</td>
<td>5.9×10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>30 min</td>
<td></td>
<td>4.42</td>
<td>0.016</td>
<td>1.474</td>
<td>3.6×10⁻³</td>
<td>8.7×10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>5.12</td>
<td>6.25</td>
<td>6.1</td>
<td>0.037</td>
<td>1.930</td>
<td>5.9×10⁻³</td>
<td>3.8×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>7.66</td>
<td>9.90</td>
<td>7.19</td>
<td>0.043</td>
<td>0.926</td>
<td>6.1×10⁻³</td>
<td>1.3×10⁻³</td>
</tr>
<tr>
<td>2-week naturally aged</td>
<td>1 hr</td>
<td></td>
<td>7.27</td>
<td>0.013</td>
<td>0.394</td>
<td>2.2×10⁻³</td>
<td>4.9×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>10.94</td>
<td>14.44</td>
<td>11.05</td>
<td>0.028</td>
<td>0.456</td>
<td>5.2×10⁻³</td>
<td>2.7×10⁻³</td>
</tr>
<tr>
<td></td>
<td>12.73</td>
<td>17.14</td>
<td>13.25</td>
<td>0.023</td>
<td>0.307</td>
<td>4.8×10⁻³</td>
<td>3.1×10⁻³</td>
</tr>
</tbody>
</table>
1. Although both needle-shape and lath-shape precipitates are present in all cases, the number densities of the laths are negligible during the early stages of aging and significantly less than the number density of $\beta''$ at the peak-age condition.

2. The ratios of the volume fractions of the needle-shape precipitates to those of the lath-shape precipitates, i.e. $\frac{f_{\text{needle}}}{f_{\text{lath}}}$, are also very large during the first hour of aging at 180°C. Although this ratio decreases by further aging to 7 hours at 180°C, the volume fraction of the needle-shape precipitates is still approximately five times larger than that of the lath-shape precipitates for the peak-age condition.

3. The number density of the needles, which increases up to 1 hour of aging, significantly decreases by continuation of aging to 7 hours at 180°C. Meanwhile, the volume fraction of the needles, which increases during the first hour of aging, has a very small increase between 1 hour and 7 hours of aging.

4. The number density of the lath-shape precipitates increases steadily during aging from 15 minutes to 7 hour at 180°C, i.e. increasing by 3.3 times. The corresponding increase in the volume fraction is considerably larger due to the fact that the average volume per precipitate is relatively large.

5. The total number density of precipitates after 7 hour of aging at 180°C is smaller than that after 1 hour of aging.

6. The sum of the volume fractions of the needle-shape and lath-shape precipitates increases significantly, from approximately 0.0021 to 0.0063, by aging from 15 minutes to 1 hour at 180°C. This value later increases to 0.0074, mainly by lath formation, for the peak-age condition.
7. The average volume per precipitate of the needle-shape precipitates increases continuously during aging from 15 minutes to 7 hour at 180°C. The average cross-sectional area, which shows small increase from 15 minutes to 1 hour of aging, almost doubles when aging continues from 1 hour to 7 hours. Although, the average length also increases between 1 hour and 7 hour of aging, the increase is not as large as that of the cross sectional area.

8. The average cross-sectional areas of the laths are very similar to those of the needles for the same aging time. The average lengths of the laths, on the other hand, are notably larger than those of the needles.

The results of the relative volume fraction estimation by TEM have been compared with the results obtained from isothermal calorimetry and DSC in Table 5.3. Clearly, good agreement is observed for times greater than 1 hour, while the TEM values are less than the corresponding calorimetry results for short times.

5.1.2 Precipitation Hardening Behaviour of the Naturally Aged Material

As in the case of the solution treated material, the following sections are categorized based on the experimental methods used for this investigation. The objective has been to obtain a better understanding for the effect of natural aging on the precipitation hardening behaviour during artificial aging. The artificial aging temperature for this study has been mainly 180°C.

5.1.2.1 Yield Strength and Hardness

Figure 5.16 shows the aging curve for a T4 sample at 180°C. The aging curve for the solution treated sample has also been included for comparison. It is observed that the yield strength slightly decreases during the first few minutes of aging and then it starts to increase, at a slow rate. The increase in yield strength after 30 minutes of aging is very small (~5 MPa). It
Table 5.3 – Comparison of the relative volume fraction of precipitates obtained by TEM, isothermal Calorimetry and DSC.

<table>
<thead>
<tr>
<th>Time at 180°C (hr)</th>
<th>TEM</th>
<th>Isothermal Calorimetry</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.28</td>
<td>0.59</td>
<td>0.65</td>
</tr>
<tr>
<td>0.5</td>
<td>0.50</td>
<td>0.77</td>
<td>0.75</td>
</tr>
<tr>
<td>1</td>
<td>0.85</td>
<td>0.89</td>
<td>0.86</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 5.16 – The aging curves for T4 and solution treated samples at 180°C.
later reaches 225 MPa, i.e. 50 MPa increase, after 1 hour of aging at 180°C. This increase in strength is only 30% of the total hardening potential of the T4 material at 180°C. The peak strength is approximately 325 MPa and it is achieved after aging for ~ 8 hours. The slow hardening kinetics for the T4 sample is better appreciated by comparing its aging curve with that of the solution treated sample. It is also evident that the peak strength is smaller (~ 15 MPa) than the peak strength of the solution treated sample.

The effect of different natural aging times on the aging behaviour has been examined by hardness tests on samples naturally aged for 3 days and 2 weeks before aging at 180°C. The results are shown in Figure 5.17. It is observed that although the starting hardness values for the two samples are different, the evolution of hardness during aging is remarkably similar. The peak hardness for both cases occurs after ~8-10 hours of aging at 180°C. Similar to the behaviour of the T4 material, the percentage of total hardening for 1 hour of aging falls in the range of 25-40%.

5.1.2.2 Electrical Resistivity

The evolution of electrical resistivity during aging at 180°C has been examined for samples naturally aged for 24 hours, 2 weeks, 3 weeks and 4 months. The results are shown in Figure 5.18. The evolution of the resistivity during aging at 180°C for the solution treated sample, is also shown for comparison. Interesting information can be deduced from this set of resistivity data by plotting them with both logarithmic, i.e. Figure 5.18(a), and linear time scales, Figures 5.18(b) and 5.18(c). The most important features of these plots are summarized as follows:

1. As expected the initial resistivities of all naturally aged samples are larger than that of the solution treated sample; also, the sample naturally aged for 24 hours has smaller starting
Figure 5.17 – The evolution of hardness during aging at 180°C of samples naturally aged for 3 days and 2 weeks.
Figure 5.18 .... continued
Figure 5.18 – The evolution of electrical resistivity during aging at 180°C for samples with various levels of natural aging. (a) logarithmic time scale, (b) and (c) linear time scales.
resistivity compared to the other naturally aged samples. This initial difference in resistivity between the 24-hour and other naturally aged samples diminish in the first minute of aging at 180°C.

2. The samples naturally aged for 2 weeks, 3 weeks and 4 months exhibit similar evolution of electrical resistivity during the entire aging period tested. The sample naturally aged for 24 hours shows similar behaviour after the first minute of aging.

3. The electrical resistivity of the 24-hour naturally aged sample increases in the first 1 minute of aging and then decreases. For all other naturally aged samples the resistivity decreases rapidly for the first few minutes. It then continues to decrease with a slower rate, Figure 5.18(b).

4. Considering the entire aging data in Figure 5.18(c), the reduction of electrical resistivity is very rapid initially. The rapid rate decreases notably after aging for 7-10 hours at 180°C.

5. The resistivity curves of the naturally aged and solution treated samples cross over after 4 hours of aging. The resistivity values for the samples naturally aged for 2 weeks and 4 months fall slightly below those of the solution treated material after this aging period. The resistivity of the naturally aged samples approach that of the solution treated sample after long periods of overaging.

5.1.2.3 Isothermal Calorimetry

Isothermal calorimetry experiments have been conducted on T4 samples at 180°C, 200°C and 220°C. The results are shown in Figure 5.19. As for the isothermal calorimetry tests of solution treated samples, no data is recorded in the first 7-10 minutes of aging. Following the stabilization of the calorimeter, exothermic heat effects are recorded in each case. The rate of heat release, i.e. $\frac{dQ}{dt}$, increases initially, reaching a maximum and then decays to zero after a
Figure 5.19 – The isothermal calorimetry traces for the T4 samples aged at 180°C, 200°C and 220°C.
characteristic aging time, \( t_f \). Although the kinetics of heat evolution is strongly dependent on the aging temperature, i.e. faster rates at higher temperatures, the total areas under the traces are similar for all three temperatures tested. The values for \( t_f \) and the total heat evolved have been tabulated along with the corresponding values for the solution treated material on page 57.

Figure 5.20 compares the isothermal traces for the T4 and solution treated samples aged at 180°C. The differences in the shapes and the total areas under the curves are remarkable. The trace for the T4 sample has a significantly smaller peak, which occurs after \(~ 45\) minutes of aging. While the total heat evolved for the solution treated sample is 11.4 J/g, that of the T4 sample is 7.8 J/g (see Table 5.1). A close examination of Figure 5.20 also shows that the heat effect for the T4 sample decays with a lower rate, resulting in a relatively longer \( t_f \) (\(~10\) hours vs. \(~4\) hours).

The calorimetry trace for aging at 180°C is compared with the evolution of yield strength for the T4 samples aged at 180°C in Figure 5.21. It is observed that the time to reach the peak strength and \( t_f \) are approximately equivalent.

5.1.2.4 Differential Scanning Calorimetry

Differential scanning calorimetry has been performed on a T4 sample to compare the behaviour of the naturally aged material with that of the solution treated sample, Figure 5.22. The important features for the T4 sample's trace are:

1. Peaks associated with the clusters and spherical GP zones are not present.
2. \( \beta'' \) peak has shifted to higher temperatures. It also has a larger heat effect than that of the corresponding peak on the trace for the solution treated sample.
3. There is a clear overlap for \( \beta'' \) and \( Q' \) peaks, i.e. \( Q' \) peak has joined as a tail to \( \beta'' \) peak.
Figure 5.20 – The isothermal calorimetry trace for the T4 and solution treated samples aged at 180°C.
Figure 5.21 – The isothermal calorimetry trace and the evolution of yield strength for the T4 samples aged at 180°C.
Figure 5.22 - The DSC thermogram for the T4 and solution treated samples.
4. An endothermic effect, i.e. trough B, is present. This trough occurs at lower temperatures and, as will be discussed in section 5.2.2.3, can be caused by a different reaction from that associated with trough A in Figure 5.11.

**DSC of Two-step Aged Samples**

Differential scanning calorimetry has been performed on samples which have been aged in two successive steps: natural aging for two weeks followed by artificial aging at 180°C for various times. The traces of the two-step aged samples are compared with the trace of a sample which has been tested after 2 weeks of natural aging without being aged at 180 °C (i.e. single-step naturally aged), Figure 5.23. The main features are summarized below:

1. Neither cluster nor SGPZ peaks are present on the DSC traces of the two-step aged samples. However a very small exothermic event centered at ~ 130°C is observed on the DSC trace for the single-step naturally aged sample.

2. The size of $\beta''$ peak reduces by aging for 30 minutes at 180°C. The peak further reduces in size after 1 hour of aging at 180°C. $\beta''$ peak is not present on the traces for the 7 hour and 24 hour aged samples.

3. $Q'$ peak is almost unchanged for the first hour of aging at 180°C. However, its height slightly reduces after aging for 7 hours and 24 hours of aging.

4. The endothermic effects, prior to the emergence of $\beta''$ peak, on the traces of the samples aged for 30 minutes and 1 hour at 180°C, are centered at ~ 210°C. This temperature is slightly higher than the center temperature of trough B (i.e. ~ 200°C). On the other hand, it is smaller than the center temperatures of trough A for the 7-hour (i.e. 225°C) and 24-hour (i.e. 240°C) aged samples.
Figure 5.23 – The DSC traces for the samples aged at 180°C after natural aging for 2 weeks. The trace for a sample naturally aged for 2 weeks without being aged at 180°C has also been included.
5. Trough A shifts to higher temperatures for the 24-hour aged sample when compared to the case of 7-hour aged sample.

The DSC traces for the samples aged for 30 minutes at 180°C with and without prior natural aging are compared in Figure 5.24. It is observed that the two traces are significantly different in terms of the size of β” peak, i.e. the naturally aged sample has a considerably bigger β” peak. In contrast, the height of Q’ peak on the trace of the naturally aged sample is smaller than that of the sample without natural aging. However, this difference is not as big as the difference in the height of β” peak.

It is also interesting to compare the precipitation states of the naturally aged and solution treated samples after aging for 7 hours at 180°C. Figure 5.25 shows the DSC traces for these two aging conditions. The two traces are very similar in general, however, a close examination shows two small differences:
1. The size of the Q’ peak is slightly larger for the solution treated sample.
2. The trough centered at ~ 230°C is wider, extending to slightly higher temperatures for the naturally aged sample.

5.1.2.5 TEM Studies

Combined DSC-TEM

In order to examine the precipitation state corresponding to the DSC peak designated as β” on the DSC trace for the naturally aged samples, TEM observations have been made on a T4 sample heated with the same rate as the DSC samples (i.e. 10°C/min) to 275°C (i.e. the approximate end temperature for this peak). The resulting microstructure has been shown in Figure 5.26. Both needle-shape β” and lath-shape Q’ precipitates are present for this heat treatment condition. However, in contrast to the case of the solution treated sample heated to
Figure 5.24 – The DSC trace for the samples aged for 30 minutes at 180°C with and without prior natural aging.
Figure 5.25 – The DSC trace for the samples aged for 7 hours at 180°C with and without prior natural aging.
Figure 5.26 – [001]_A bright field TEM micrograph for the T4 sample ramp heated (10°C/min) to 275°C. TEM observations by A. Perovic
260°C, the number density of the Q' precipitates appears to be larger than that of the needle-
shape precipitates.

Evolution of Microstructure during Aging at 180°C

Quantitative TEM studies have also been conducted on the samples aged for 1 hour, 7
hours and 24 hours at 180°C after natural aging for 2 weeks (i.e. two-step aged). Both needle-
shape and lath-shape precipitates are observed in all three cases of aging at 180°C. The results of
the quantitative measurements are summarized in Table 5.2, along with the results for the
solution treated samples aged at 180°C. The main features of these observations are:
1. The average volumes per precipitate for both the needle-shape and lath-shape precipitates
   increase continuously during aging from 1 hour to 24 hours at 180°C.
2. The sizes of both types of precipitates, i.e. cross-sectional area and length, are larger than
   those for the solution treated samples aged for the same periods at 180°C.
3. The number densities of both needle-shape and lath-shape precipitates are smaller than the
   corresponding number densities for the solution treated material.
4. Although the volume fractions of the needle-shape precipitates are smaller, the volume
   fractions of the lath-shape precipitates are larger for the naturally aged samples compared to
   the corresponding values for the solution treated samples. Hence, the \( \frac{f_{\text{needle}}}{f_{\text{lath}}} \) values for the
   naturally aged samples are smaller than the corresponding values for the solution treated
   sample for both cases of 1 and 7 hour of aging.
5. The number density of the needles increases up to 7 hour of aging. It then decreases
   significantly by aging to 24 hours at 180°C. So does the volume fraction, although the
decrease in the volume fraction is less severe.
6. The number density of the laths increases up to 7 hour of aging. It then decreases slightly by aging to 24 hours at 180°C. The volume fraction of the laths, however, increases continuously from 1 hr to 24 hour of aging.

7. The sum of the volume fractions of the needle-shape and lath-shape precipitates increases from approximately 0.0027 to 0.0079 by aging from 1 hour to 7 hours at 180°C. This value, which is very similar to the corresponding value for the solution treated material, remains unchanged for the sample aged for 24 hours.

8. The sum of the number densities of the needles and laths decrease by aging from 7 to 24 hours.

5.2 Discussion

5.2.1 Precipitation Hardening of Solution Treated Material during Artificial Aging

5.2.1.1 Evolution of Yield Strength

The evolution of yield strength can be related to the kinetics of precipitation as well as the type of the zones and precipitates that form during aging. The large age hardening response and similar peak strength for the cases of aging in the temperature range of 140-220°C suggest that the precipitation processes for this temperature range are similar. Hence, based on the information obtained for the microstructural evolution during aging at 180°C (i.e. TEM and DSC studies), it may be concluded that β'' is the main hardening phase that forms during aging in this temperature range. However, other metastable phases, such as spherical GP zones and Q' can also be found over this temperature range. This can be examined using a schematic metastable phase diagram (assuming a pseudo-binary system) as shown in Figure 5.27. According to the knowledge obtained through DSC and TEM experiments, aging of the solution treated material at 180°C may be represented by the case of T₁ in Figure 5.27. On the other hand, when the aging
Figure 5.27 – A schematic pseudo-binary metastable phase diagram (Al-rich corner) suggested for AA6111.
temperature is above the solvus boundary for spherical GP zones, these zones will not form and
the microstructure may consist of β" and Q', depending on the temperature and the extent of
aging. The change in precipitation hardening behaviour at 220°C, observed in isothermal
calorimetry experiments, may be attributed to the relative proximity of 220°C to the metastable
solvus temperature for β", e.g. T₂ on the schematic phase diagram. It has been shown that the
peak strength for aging at 220°C is reached when the relative volume fraction of precipitates is ~
95% (see Figure 5.10). The peak strength is also slightly lower for aging at 220°C, compared to
aging at lower temperatures (~330 MPa vs. 335-340 MPa for the lower temperatures in the
range). These observations indicate that there are differences in the precipitation process for the
higher aging temperature, particularly for aging conditions close to the peak. It may be
speculated that the lower peak strength for aging at 220°C is due to a smaller ratio \( \frac{f_{\alpha'}}{f_Q} \)
compared to the corresponding ratios at lower temperatures.

Considering the case of aging at 250°C, the different response compared to aging at
lower temperatures may also be explained in terms of the type of phases present in the
microstructure. Although aging at a relatively higher temperature may result in a smaller volume
fraction of precipitates (according to the shape of the phase diagram and the inverse lever rule),
the large difference in the peak strength indicates that much higher proportion(s) of Q', or other
Q phase variants, may form for the case of aging at 250°C. Hence, on the schematic phase
diagram, 250°C may be notably above T₂ (e.g. T₃ where β" does not form).

Returning to the particular cases of aging at 180°C and 20°C, the rapid kinetics of
hardening during the first hour of aging at 180°C can be readily explained by the corresponding
fast kinetics of precipitation (Figure 5.10). It is also clear that the peak strength is reached upon
the completion of β" precipitation (see Figure 5.11 and Table 5.2). For the case of aging at
20°C, the proposed logarithmic relationship is consistent with the relationship suggested by Lloyd and Gupta [1997]. The small differences in the coefficients of the relationship between the present work (equation 5.1) and that of Lloyd and Gupta arises probably from small differences in the chemistry of the two alloys and the natural aging time over which the logarithmic fit has been applied.

5.2.1.2 Evolution of Electrical Resistivity

It is well known that all factors tending to disrupt the regularity of the metal lattice tend to increase its resistivity [Stanley 1963]. Solute atoms produce distortions in the lattice and therefore cause scattering of the conduction electrons, leading to an increase in the electrical resistivity. According to Matthiessen's law electrical resistivity, \( \rho \), can be described as:

\[
\rho = \rho(T) + \sum_i \rho_i c_i
\]  

(5.7)

where \( \rho(T) \) is the temperature dependent thermal contribution to electron scattering, \( c_i \) is the solid solution content of an element and \( \rho_i \) is the corresponding resistivity coefficient. For aging of a quasi-binary alloy Matthiessen's law can be re-written as:

\[
\rho_t = \rho(T) + \rho_a C
\]  

(5.8)

where \( \rho_t \), \( \rho_a \) and \( C \) are the resistivity at time \( t \), resistivity coefficient for the solute and the concentration of solute in the matrix at time \( t \), respectively. \( \rho(T) \), which is the resistivity of the pure Al at the measuring temperature, is constant. Rearranging equation (5.8):

\[
\rho_t - \rho(T) = \rho_a C
\]  

(5.9)

Therefore the resistivity change during aging is proportional to the change in the solute concentration. According to the above equation, resistivity should decrease as the matrix is depleted of solute atoms during the precipitation process. However, in many precipitating systems, the initial decomposition of solid solution is accompanied by an increase in resistivity.
The resistivity increases during initial stages of aging, reaches a maximum, and then decreases by further aging for longer times. This behaviour is often referred to as the "resistivity anomaly" [Kelly and Nicholson 1963]. The resistivity anomaly is usually described according to the so-called "RW" (Rossiter-Wells) and/or "HEW" (Hillel-Edwards-Wilkes) theoretical models [Rossiter and Wells 1971, Rossiter 1976, Hillel et al. 1975, Edwards and Hillel 1977, Hillel 1983].

For spherical GP zones in a binary system, the HEW theory during the early stages of zone formation, i.e. when the size of the zones is small, is simplified as [Hillel et al. 1975]:

\[
p = p(T) + (C_a - ZN)p_a + Zp_N
\]

where \(C_a\) is the total solute concentration, \(Z\) is the number density of GP zones, \(N\) is the number of atoms per zone, \(p_a\), as before, is the resistivity coefficient of the solute and \(p_N\) is the resistivity coefficient for the GP zone. For late stages of aging when the GP zones have a very large size, the HEW model further simplifies and reduces to Matthiessen's law:

\[
p = p(T) + (C_a - ZN)p_a
\]

Based on the HEW theory, Osamura et al. [1982] have described the origin of the resistivity anomaly in an Al-4wt\% Cu alloy, assuming that GP zones consist of a single layer of Cu atoms. According to their view, the resistivity anomaly can be easily understood by considering that the conductivity of the alloy during aging is the sum of two partial conductivities. As the precipitation proceeds, one partial conductivity increases due to the depletion of solutes from the matrix. The other partial conductivity decreases because of the GP zone growth. The combination of both conductivities produces a minimum, or in other words, a maximum in resistivity. This description by Osamura et al. [1982] is also implied by the simplified relationship (5.10).
The origin of the resistivity anomaly in the present case may also be described on the basis of the above theories. This can be the subject of interesting future work, combining various characterization techniques such as atom probe and high resolution electron microscopy with the theoretical analysis. As stated by Hillel and Rossiter [1981], any complete treatment of the effects of alloy decomposition on the electrical resistivity should incorporate the effects of a combination of factors such as the structure of clusters and the cluster-matrix interface, particle-size broadening and anisotropy in the Bragg scattering of the clusters. However, the existing knowledge on the precipitation behaviour of the present alloy and the simplified relationship (5.10) can be used to explain the resistivity maximum/plateau (Figure 5.3) on the basis of the resultant effects of solute depletion and zone formation.

The observed transition from fast to slow reactions (corresponding to the aging time $t_a$) can be understood according to the model proposed by Federighi and Thomas [1962]. The transition from a fast to a slow reaction is believed to be due to the binding energies between vacancies and the solute clusters. During the fast reaction, the clusters form at a rate governed by the concentration of excess vacancies. The rate then rapidly declines as the vacancies become trapped in the growing clusters. The subsequent slow reaction is controlled by the low concentration of vacancies in the matrix [Panseri and Federighi 1966]. The activation energy, which has been found for the fast process in the present alloy, i.e. 38 KJ/mole (0.4 eV), is very similar to the activation energy for the migration of vacancies in aluminum after quenching from 550°C, i.e. 0.42±0.02 eV [Panseri and Federighi 1958] (recalling that the quenching temperature for the present study has been 560°C). Similar activation energies have also been reported for the first DSC peak (attributed to clustering events) for AA6061 i.e. 33.1±7.5 KJ/mole, [Dutta and Allen 1991] as well as the first peak of the differential thermal analysis (DTA) for Al-0.92wt%Mg-0.93wt%Si alloy, i.e. 0.41 eV, [Barczy and Tranta 1975]. However, it is different
from the activation energy of the fast process estimated from the electrical resistivity measurements by Panseri and Federighi [1966] (i.e. 0.75 eV) on Al-0.9wt%Mg-0.51wt%Si alloy. This discrepancy may be related to difference in the chemistry of the alloy used by Panseri and Federighi with 6111 and the above mentioned alloys.

This finding is consistent with the early as well as more recent views expressed for the presence of high concentrations of vacancies in the clusters and zones, [Lutts 1961, Panseri and Federighi 1966, Murayama and Hono 1999, Bryant 1999]. Recalling that the activation energy for the fast process has been found from the aging data at the temperature range of 20-120°C, the presence of vacancy enriched clusters are readily acceptable for the low temperature clustering/zone formation. Considering the results of the studies of Panseri et al. [1958] on the interaction between solute Mg atoms and vacancies in aluminum, the trapping of vacancies in the clusters/zones at temperatures above 120°C may be less likely. Hence, the clusters and zones that form at higher temperatures may have smaller concentrations of the vacancies, depending on the temperature. This view is also in agreement with the suggestions by Edwards et al. [1998] and Murayama and Hono [1999].

**Aging at 180°C**

As it will be discussed in section 5.2.1.3, it is suggested that the microstructure associated with the resistivity anomaly, which occurs for 5 minutes of aging at 180°C, comprise of spherical GP zones, β” and Q’. Although the proportion of Q’ should be very small and some clusters may also exist. Considering the theoretical resistivity models, one or more of these precipitates should have high electron scattering potential(s) to cause the initial increase in the resistivity [Hillel and Rossiter 1981]. As shown before (Figure 5.9), the relative volume fraction of precipitates for 5 minutes of aging at 180°C is ~ 30%. Hence, a substantial fraction of the
solutes have been depleted from the matrix when the resistivity reaches the maximum point.
Thus according to equation (5.10), the resistivity increase may be attributed to the conditions
where the increase in resistivity due to the growing precipitates counterbalances the decrease in
the resistivity due to the solute depletion. The resistivity reaches a maximum when this balance
reverses.

It is of interest to examine the applicability of equation (5.9), i.e. Matthiessen' law, to the
resistivity data beyond the maximum resistivity. To be able to do so, the change in resistivity
should be related to the decrease in the solute concentration during aging. Following Shewmon
[1963] and Shercliff and Ashby [1990], the change in the solute concentration in the matrix
during precipitation is described by the following exponential decay function:
\[ C_i = C_e + (C_i - C_e) \exp(-kt) \] (5.12)
where \( C_i \) is the initial solute concentration, \( C_e \) is the solute concentration at equilibrium at the
aging temperature, and \( k \) is the temperature dependent rate constant. Now according to equation
(5.9) if the resistivity change follows Matthiessen’s law, it should also show an exponential
decay relationship with time, similar to equation (5.12). Replacing \( C_i \) in equation (5.9):
\[ \rho_i - \rho(T) = \rho_a C_e + \rho_a (C_i - C_e) \exp(-kt) \] (5.13)
\( \rho_a C_e = \rho_e \) is the contribution to resistivity by the solutes at equilibrium. In the present context
\( \rho_e \) can be regarded as the resistivity contribution from solutes when the precipitation process is
complete. Rearranging equation (5.13):
\[ \rho_i = \rho(T) + \rho_e + \rho_a (C_i - C_e) \exp(-kt) \] (5.14)
The sum of the contributions from the pure Al matrix, \( \rho(T) \), and \( \rho_e \) is the resistivity of the
material when the precipitation reactions are complete, i.e. \( \rho^* \):
\[ \rho^* = \rho(T) + \rho_e \] (5.15)
Replacing equation (5.15) in equation (5.14):

\[ \rho_i = \rho^* + A \exp(-kt) \]  \hspace{1cm} (5.16)

where \( A = \rho_a (C_i - C_e) \). Equation (5.16) is now fitted to the resistivity data for the period of 5 minutes (i.e. where \( \rho \) is maximum) to 4 hours (where the slope of the resistivity starts to change and it corresponds to the peak-age condition). The results of the fit are compared with the experimental data in Figure 5.28. An excellent agreement between the fitted values and experimental data is observed. The fitted equation is as follows:

\[ \rho_i = 16.93 + 2.25 \exp(-3.5 \times 10^{-4} t) \]  \hspace{1cm} (5.17)

where the units of resistivity and time are n\(\Omega\)m and second, respectively. It is therefore seen that the resistivity data for the solution treated material, aged at 180°C, in the time period between the resistivity maximum and the peak-age condition can be very well described by an exponential decay function.

Despite the apparent applicability of Matthiessen’s law during the aging period between the time to the resistivity maximum (i.e. 5 minutes) and the peak-age condition (i.e. 4 hours), the small precipitates/GP zones may significantly contribute to the electron scattering effects well beyond 5 minutes of aging at 180°C. This effect will, however, decrease as the precipitates become larger during aging, until they attain large enough sizes for which electron scattering effects are negligible. The electron scattering effects due to small precipitates/GP zones, thus, tend to reduce the exponential decay rate, when compared to a condition where the resistivity decrease is solely due to the solute depletion (Matthiessen’s law). Having known this effect, as well as the initial solute depletion during the first 5 minutes of aging (~ 30%), the rate constant in equation (5.17) cannot be directly used to obtain the fraction of solutes depleted (or the relative volume fraction of precipitates) during the entire underaging period at 180°C. However,
Figure 5.28 – The resistivity data during underaging for the solution treated sample. The data beyond the maximum resistivity follows an exponential decay function.
the method is expected to be directly applicable for determination of the kinetics of solute
depletion and precipitation for the cases where the resistivity anomaly is not observed or is
negligible (e.g. aging above 200°C in AA6111, see also Jo and Fujikawa [1993] for aging of Al-
Sc alloys). For the cases where the anomaly is significant, e.g. aging at 180°C, more
investigation is in process to relate the kinetics of precipitation (which is also attainable from
isothermal calorimetry) to the kinetics relationship obtained from the above resistivity analysis.

The resistivity change during the overaging condition is significantly slower than the
change up to the peak-age condition. To examine the applicability of equation (5.16) to the
overaging condition, the relationship has been fitted to the resistivity data in the time interval of
4 to 191 hours. The following relationship has been obtained:

$$\rho_f = 15.41 + 1.56\exp(-5.6\times10^{-6}t)$$

(5.18)

where the units of resistivity and time are nΩm and second, respectively. The good agreement
between the above fitted relationship and the experimental data is evident from Figure 5.29. Hence,
the solute depletion in the overaging regime may also be described by a decaying exponential function. Comparing equation (5.18) with equation (5.17), it is obvious that the rate
of solute depletion is considerably slower in the overaging period, as the rate constant $k$ is
approximately 63 times smaller for overaging when compared to the underaging condition.

As shown in Figure 5.12, overaging for the present alloy may be accompanied by slow
phase transition processes (some of which may occur in the grain boundaries). The TEM results,
on the other hand, provide direct evidence for the coarsening processes during overaging. It is
generally accepted that coarsening is accompanied by a small decrease in the residual
It is, therefore, suggested that the solute depletion during overaging in the present alloy, which is
well described by an exponential decay function, may be caused by both coarsening and phase
Figure 5.29 – The resistivity data during overaging can be described by an exponential decay function for the aging interval of 4-191 hours at 180°C.
transition processes.

**Aging at 20°C (Natural Aging)**

The large increase in resistivity during aging at 20°C suggests that the natural aging clusters/zones have high potential of scattering the conduction electrons. The evolution of resistivity during natural aging (Figure 5.3) shows that the resistivity reaches a plateau after 30 days, however no resistivity increase or decrease is observed even after 160 days of natural aging. Figure 5.30 compares the trends in the evolution of the electrical resistivity and the yield strength. It is clear that although the resistivity does not change after 30 days of natural aging, the yield strength continuously increases with natural aging (2 years tested). The increase in yield strength suggests that clusters/zones continue to form/develop during natural aging. The fact that the resistivity does not decrease by continuation of natural aging, on the other hand, implies that these clusters do not grow continuously and they retain their fine sizes, or in other words, their high electron scattering potential. The resistivity plateau, therefore, can be understood in terms of the opposite effects of the formation of fine clusters/zones and the associated solute depletion from the matrix (equation 5.10). This interpretation suggests that the formation of the clusters/zones during the late stages of natural aging is governed by a very slow nucleation process and the growth of these nuclei is very limited. The evolution of the volume fraction of the clusters/zones during natural aging has been modeled. The model will be presented in Chapter 6 (section 6.3.4.1).

Zhuang et al. [2001] have shown that the natural aging clusters in an AA6016 alloy have a diameter of ~ 0.6 nm after 2 hours of natural aging. The size of these clusters then increase to 1-2 nm after ten hours of natural aging, after which it remains constant for two weeks of natural aging. Zhuang et al. suggest that, after the initial rapid growth, these clusters do not grow by further natural aging. However, they become more enriched with the solute atoms. Murayama
Figure 5.30 – The evolution of electrical resistivity and yield strength during natural aging.
et al. [2001] and Matsuda et al. [2000] have also found clusters of ~ 2 nm diameter after 7 days of natural aging and ~ 1 nm in diameter after 60 ks (16.7 hours) of natural aging, respectively, in the alloys of their investigation. In the present work, the TEM studies on samples with different natural aging times, have not shown any evidence for these clusters [Wang 2001]. Neither have the TEM studies by Miao and Laughlin [2000b] on the naturally aged 6111 samples, implying that the clusters are not resolvable by conventional TEM. Based on all the above information, the suggestion of Zhuang et al. [2001] on the limited growth of these clusters during the very early stages of natural aging (a few hours), and the basically constant average size beyond those very early stages, seems reasonable.

5.2.1.3 Precipitation Behaviour

Precipitation Kinetics

Precipitation processes release heat and hence give rise to exothermic heat evolution during isothermal calorimetry runs. The rate of heat release increases first, reaches a maximum and then decays to zero with the continuation of aging (Figure 5.7). Considering the very short duration of $\Delta t$ (see Table 5.1) and the shapes of the traces (i.e. sharp maxima) for aging at 180°C, 200°C and 220°C, it seems that precipitation processes start earlier than $t_0$ for these high temperature experiments. However, due to the short duration of $t_0$ compared to $t_f$, the data lost for the heat evolution prior to $t_0$ is a very small fraction of the total heat evolved for the temperature range investigated. Hence, the relative volume fractions estimated according to equation (5.4) can be considered as reasonably good approximations to the true values. The relatively longer $\Delta t$ for the case of aging at 160°C is related to a slower kinetics at a lower temperature.
The similarity between the time to reach the peak strength and $t_f$ implies that the precipitation of hardening phases approaches completion for this aging time. Moreover, the observation of similar total areas under the isothermal calorimetry traces implies that the total volume fractions of the precipitates are similar at the peak-age for the temperature range of 160-220°C. This in turn may imply that the apparent metastable solvus lines for the phases present at the peak, i.e. $\beta''$ and $Q'$, are relatively steep in this temperature range.

**Evolution of Microstructure during Aging at 180°C**

The details of the evolution of microstructure during aging at 180°C can be well examined by considering the DSC and TEM results (sections 5.1.1.4 and 5.1.1.5). Returning to DSC results (see Figure 5.11), the absence of the peak associated with clusters on the traces for all samples aged at 180°C, including 5 minutes aging, indicates that the clusters/zones either form during the first 5 minutes at 180°C or they do not form during aging at 180°C. Interestingly, the peak attributed to the spherical GP zones (SGPZ), which is not very clearly noticed on the DSC trace for the solution treated sample (see also Figure 2.1a), is readily observable on the DSC traces for the samples aged for 5 and 15 minutes at 180°C. It appears that these precipitates form continuously during aging for 30 minutes at 180°C. The reason that the height of the SGPZ peak appear almost unchanged for the first 5 minutes of aging, but at the same time the height of $\beta''$ peak reduces considerably, is possibly due to the overlaps between the SGPZ and $\beta''$ peaks. Hence, part of the decrease in the height of $\beta''$ peak probably comes from the formation of spherical GP zones. Considering also the slight decrease in the height of $Q'$ peak, it is inferred that all three types of precipitates, namely spherical GP zones, $\beta''$ and $Q'$ should be present, although probably very small in size, in the microstructure of a solution
treated sample aged for 5 minutes at 180°C (corresponding to the resistivity maximum). The clusters may or may not be present for this condition of aging.

The DSC results for samples aged for 15 and 30 minutes at 180°C provide clear evidence that the microstructure consist of spherical GP zones, β” and Q’. Hence, the needle-shape and lath-shape precipitates observed on the TEM micrographs of the samples aged for 15 and 30 minutes at 180°C are β” and Q’. Despite the DSC evidence, the spherical GP zones have not been resolved by the present conventional TEM studies. This indicates that the total volume fraction of precipitates for 15 minutes and 30 minutes of aging should be higher than the sum of the volume fractions of β” and Q’ shown in Table 5.2. It is for this reason that, the relative volume fractions obtained by TEM for 15 minutes and 30 minutes of aging are smaller than the relative volume fractions obtained by the analysis of the isothermal calorimetry and DSC data (see Table 5.3). The data in Table 5.3 suggests that approximately one half of the precipitates in the microstructure of the sample aged for 15 minutes at 180°C consists of spherical GP zones. This proportion reduces by further aging for 30 minutes at 180°C. The DSC trace for the sample aged for 30 minutes at 180°C suggests that the formation of spherical GP zone approaches completion after 30 minutes of aging at 180°C.

The DSC trace of the 30 minute-aged sample shows the endothermic trough A in the temperature range of 185-250°C. This is due to the dissolution of those precipitates which have formed during 30 minutes of aging at 180°C and are now unstable during the DSC run when the temperature rises above 180°C [Lloyd et al. 2000]. The presence of this negative heat effect counterbalances some of the positive heat effects due to β” formation and therefore the size of the β” peak become very small. The same is true for the DSC trace of the sample aged for 1 hour at 180°C. This means that some β” may still form after 1 hour of aging at 180°C. However, considering the results of the quantitative TEM analysis, where it shows very little
change in the volume fraction of $\beta''$ between 1 hour and 7 hours of aging, $\beta''$ precipitation should approach completion soon after 1 hour of aging at 180°C. The microstructure of the 1 hour-aged sample, according to both DSC and TEM results, comprise of $\beta''$ and $Q'$ precipitates, although the proportionality of $\frac{f_{\beta''}}{f_{Q'}}$ is very large (see Table 5.2).

The TEM results for 7 hours aging at 180°C, indicate that the microstructure comprise $\beta''$ and $Q'$ precipitates, both larger in size compared to the case of 1 hour aging at 180°C (see Figure 5.15 and Table 5.2). The decrease in the number density of $\beta''$ between 1 hour and 7 hours of aging, while the volume fraction has slightly increased, may be attributed to coarsening. However, the coarsening process may also be accompanied by a gradual phase transition from $\beta''$ to $Q'$. Close examination of the DSC trace for the 7 hour-aged sample shows that the size of the $Q'$ peak is roughly equal to the size of trough A. In other words, the summation of the two positive and negative heat effects is almost zero (see also section 5.1.1.4). This may suggest that $\beta''$ precipitates, and probably the smaller $Q'$ precipitates, that have formed during aging for 7 hours at 180°C, dissolve during the DSC run at a temperature range of 180-260°C. The dissolved solutes then form new $Q'$ precipitates at a higher temperature range.

Considering the DSC traces for the overaging regime (see Figure 5.12), it is observed that the overaging reactions consist of phase transitions involving $Q$ phase and its variants. The possible transition from $\beta''$ to $Q'$ is not observable as a change in an exothermic peak, but as in the case of the sample aged for 7 hours at 180°C, this effect is probably associated with the large endothermic event starting at $\sim$ 180°C and extending to the onset of the peaks associated with $Q$ and its pre-cursors (i.e. trough A). The shift of trough A to higher temperatures during overaging implies that the precipitates formed during overaging at 180°C become continuously larger, hence, provides an indirect evidence for the coarsening during overaging.
Direct evidence for coarsening during aging comes from the TEM results. As listed in Table 5.2, the quantitative TEM analysis shows that the number density of β'' as well as the total number density of precipitates decrease between 1 hour and 7 hour of aging for the solution treated material. Also the number density of precipitates decrease between 7 hour and 24 hour of aging, while the volume fraction remains unchanged, for the case of the naturally aged material. The decrease in the number densities in each case is accompanied with the increase in size of the precipitates. Moreover, the TEM work by Gupta et al. [2000] on a solution treated 6111 sample aged for 168 hours at 180°C has shown that β'' particles with relatively large end-on views are still present in the microstructure. Recalling from the DCS results that no β'' forms after 7 hour of aging, the coarsening of β'' seems a potential process during overaging. All the above observations indicate that coarsening processes involving both β'' and Q' occur during overaging.

5.2.2 Precipitation Hardening of Naturally Aged Material during Artificial Aging

5.2.2.1 Evolution of Yield Strength during Aging at 180°C

The initial drop in yield strength of the T4 sample during aging at 180°C (Figure 5.16) is related to the dissolution of the natural aging clusters/zones. This view is supported by the DSC observation of the large endothermic event designated as trough B (Figure 5.22), which is attributed to the dissolution of clusters formed during natural aging [Lloyd et al. 2000]. It is also consistent with the view presented by Murayama and Hono [1999] that the small size co-clusters formed during natural aging revert during aging at 175°C. The slow kinetics of hardening for the naturally aged sample during aging at 180°C should then be related to the presence and dissolution of these clusters. The observation of similar times for the peak strength and the decay of the isothermal calorimetry trace to zero heat flow (Figure 5.21), as in the case of the
solution treated sample, indicate that the precipitation of hardening phases approach completion at the peak-age condition.

The early research of Pashley et al. [1966] on naturally aged Al-Mg-Si(-Cu) alloys provides important information on the effect of the variation in the natural aging times on the artificial aging response. In the Cu-free alloy of their investigation, natural aging time as low as 30 minutes lower the aging response when the sample is aged for 16 hours at 175°C. The reduction in the aging response increases by increasing the natural aging time to 8 hours. Further increase in the natural aging time, up to 20 days, does not cause any additional reduction in the artificial aging response [Pashley et al. 1966]. In the Cu-bearing alloy, the reduction in the artificial aging response (16 hours at 175°C) starts after the sample is naturally aged for 1 hour. This reduction increases by increasing the natural aging time to 24 hours, after which no further reduction in the artificial aging response is observed [Pashley et al. 1966]. More recently, a similar observation on an Al-Mg-Si alloy has been reported by Uchida and Yoshida [1996]. They have shown that the paint bake response, PBR (30 minutes at 170°C), is continuously reduced by increasing the natural aging time up to 1000 minutes. Further increasing of the natural aging time has shown no further significant change in PBR. The present hardness results on 3-day and 2-week naturally aged samples are consistent with the above studies. It also provides an evidence that the delay in the peak strength of the naturally aged samples during artificial aging (compared to that of the solution treated sample), is also independent of the natural aging time, within the range of 3 days two years of natural aging. Moreover, it shows that the kinetics of hardening for the samples with the two different levels of natural aging is very similar. This implies that the kinetics of precipitation of the hardening phases are very similar for the two cases.

The slow rate of hardening is attributed to the effect of the natural aging clusters on altering the nucleation mechanisms during artificial aging. Having formed clusters/zones during
natural aging, the supersaturation of the matrix for the naturally aged material is reduced. Hence the driving force for nucleation, and hence the nucleation rate, in the case of the naturally aged material is smaller than that of the solution treated (i.e. as-quenched) material. Also, considering that the natural aging zones are clusters and/or co-clusters of Mg and Si (section 2.3.2), the proportionality of the concentrations of Mg, Si and Cu in the matrix of the naturally aged material is different from that of the as-quenched material (i.e. more Cu is available for a specific concentration of Mg or Si). This effect, combined with the reduced driving force for the nucleation of $\beta''$, can result in enhanced nucleation of $Q'$ in the case of the naturally aged material. This view has been verified by the experimental observations, as will be discussed in more detail in section 5.2.2.3. It should also be mentioned that the kinetics of growth for the nuclei of $Q'$ may be different from that of $\beta''$. In addition to the above differences, the natural aging zones alter the nucleation process by having occupied the potential nucleation sites for precipitates forming during artificial aging. This effect has also been evidenced by the coarser microstructure in the case of the artificially aged naturally aged material (see section 5.2.2.3).

A plausible explanation can be given for the similarities in the kinetics of hardening for the samples with various levels of natural aging based on the similar sizes of the natural aging zones for those various levels of natural aging. As will be discussed in Chapter 6 (section 6.3.1.1), similar average sizes of the natural aging clusters (regardless of the natural aging level) at the beginning of the artificial aging process suggests similar dissolution kinetics for these clusters. Now, if the nucleation and growth of the new precipitates depend on the dissolution of these clusters, similar dissolution kinetics will lead to similar precipitation kinetics during artificial aging. The slow rates of hardening may then be caused by both the decrease in the driving force for the precipitation of $\beta''$ and the slow rates of dissolution of the natural aging clusters.
5.2.2.2 Evolution of Electrical Resistivity during Aging at 180°C

The initial rapid drop in the resistivity of the 2-week, 3-week and 4-month naturally aged samples during aging at 180°C can be explained in terms of the opposite effects of the dissolution of natural aging clusters and the formation of very fine new precipitates. The former process decreases the resistivity by decreasing the term “$Z\rho_N$” in equation (5.10) (i.e. $\rho = \rho(T) + (C_a - ZN)\rho_a + Z\rho_N$). In contrast, the formation of very fine nuclei of the new precipitates increases the resistivity by increasing the “$Z\rho_N$” term in equation (5.10). The two processes are also accompanied by solute enrichment and depletion in the matrix, respectively. The net effects of these processes cause a rapid drop in the resistivity. Considering the slow precipitation kinetics, resulting in slow solute depletion, the considerable initial drop in resistivity implies that the electron scattering potential of the natural aging clusters exceeds that of the newly formed fine precipitates. This is in agreement with the observation of significantly larger resistivity anomaly for aging at 20°C, compared to that for aging at 180°C (see Figure 5.3).

The initial increase in the resistivity of the 24-hour naturally aged sample during aging at 180°C can also be explained based on the counteracting effects of dissolution and precipitation processes described above. In this case, since the volume fraction of the natural aging clusters is smaller than those naturally aged for the longer times, less clusters dissolve during the same period of aging, i.e. smaller decrease in “$Z\rho_N$” in equation (5.10). The net effect then causes the resistivity to rise in the first minute of aging at 180°C.

In order to examine the applicability of Matthiessen’s law to the resistivity data for the artificial aging of naturally aged samples, equation (5.16) was fitted to the experimental data for the aging period of 3 minutes to 7 hours, excluding the very initial as well as the overaging periods. Excellent agreements have been found between the experimental results and the fitted
values, as shown in Figure 5.31, for the 2-week naturally aged sample. As expected from the similarities in the resistivity curves, the samples with various levels of natural aging show similar kinetics of resistivity change. The following relationships are found for the samples with various levels of natural aging (resistivity in \( \text{n}\Omega\text{m} \) and time in s):

24 hours natural aging:  
\[ \rho_t = 16.03 + 4.69 \times 10^{-5} \exp(-8.3 \times 10^{-5} t) \]  
(5.19)

2 weeks natural aging:  
\[ \rho_t = 15.31 + 5.39 \times 10^{-5} \exp(-6.4 \times 10^{-5} t) \]  
(5.20)

4 months natural aging:  
\[ \rho_t = 15.39 + 5.37 \times 10^{-5} \exp(-7.8 \times 10^{-5} t) \]  
(5.21)

The observed behaviour for the evolution of resistivity during aging at 180°C for the naturally aged materials, can be interpreted as follows. The electron scattering effects due to the natural aging clusters reduce as a result of dissolution, i.e. \( Zp_N \) term in equation (5.10) decreases. On the other hand, the newly formed fine precipitates increase \( Zp_N \) term. It is also possible that the newly formed precipitates do not have large electron scattering potentials (due to the different proportion of phases, compared to the case of the artificial aging of solution treated material). Hence, the two effects may or may not compensate for each other during aging. In any case, the effect of natural aging clusters will reduce to zero by approaching the complete dissolution during aging. The possible scattering effects of the newly formed small precipitates will also decrease as the precipitates become larger and the nucleation rate decreases. Considering all effects on the resistivity evolution, equations (5.19)-(5.21) reflect the net effects of all possible reactions, namely cluster dissolution, small precipitate formation, solute enrichment due to the dissolution of the clusters and solute depletion due to precipitation. The observed continuous decrease in the resistivity during aging indicates that the factors that cause the resistivity to decrease (i.e. cluster dissolution and solute depletion) surpass the total effects that tend to increase the resistivity (i.e. solute enrichment due to the cluster dissolution and the
Figure 5.31 – The resistivity data during underaging, beyond the first 3 minutes, for the 2-week naturally aged sample follows an exponential decay function.
scattering effects of newly formed small precipitates). The above interpretation, thus, suggests that equations (5.19)-(5.21) do not directly provide the rate of solute depletion due to precipitation. Further studies are in process to deconvolute the above combined effects and to obtain the kinetics information on the dissolution of clusters and precipitation of new phases during artificial aging. The kinetics of cluster dissolution and precipitate formation during artificial aging of the naturally aged materials have also been obtained through the analysis of isothermal calorimetry results on T4 samples. The analysis will be presented in Chapter 6, and the similarities and differences between the results obtained from the two methods of calorimetry and resistivity will be discussed (section 6.3.1.1).

As in the case of the solution treated sample, the overaging data can also be described by an exponential decay relationship, Figure 5.32. The interpretation of concurrent coarsening and phase transition effects, which has been suggested for the overaging of the solution treated sample is also proposed for this case. The relationship that describes the resistivity change during overaging between 10 and 191 hours of the 2-week naturally aged sample is as follows:

$$\rho_t = 15.12 + 1.13 \exp(-5.6 \times 10^{-6} t)$$

(5.22)

Comparison of equation (5.22) with equation (5.18) reveals that the kinetics of overaging for both 2-week naturally aged and solution treated samples are similar for similar overaging periods. It is recalled that the starting time for fitting equation (5.16) to the experimental data for both cases have been the start of the overaging processes, i.e. when the resistivity reduction rate drastically decreases (i.e. 10 hours for the naturally aged sample and 4 hours for the solution treated sample).
Figure 5.32 – The resistivity data for the 2-week naturally aged sample during overaging can be described by an exponential decay function for the aging interval of 10-191 hours.
5.2.2.3 Precipitation Behaviour

Precipitation Kinetics

Tensile and DSC results on the T4 samples have previously suggested that the clusters formed during natural aging undergo dissolution during artificial aging, although the extent of the dissolution process has not been clarified, yet. More information on the dissolution of these clusters has been learned from the isothermal calorimetry experiments on the T4 samples. Considering the features of the isothermal calorimetry traces for the T4 samples (when compared to the traces for the solution treated material aged at the same temperature), e.g. shape and the small total heat evolution, enlightens the idea that the observed traces are the net effects of concurrent dissolution and precipitation processes. More precisely, a dissolution process, which should have an endothermic effect, absorbs some of the heat that is released by the precipitation process. Hence, the observed trace is the net effect of two processes having heat effects of opposite signs. Therefore the total heat evolution is considerably smaller than that of the solution treated sample aged at the same temperature. According to this view, the peak on the isothermal trace for the T4 material is produced as a result of the addition of the two endothermic and exothermic heat flows. This concept, which has been schematically shown in Figure 5.33, has been used in the next chapter to model the precipitation and dissolution kinetics for artificial aging of the naturally aged material. The results of the proposed model reveal the slow rates of dissolution for the clusters as well as the slow rates of precipitation during artificial aging of the naturally aged material.

Evolution of the Microstructure of the T4 Material during the DSC Run

The precipitation behaviour of a naturally aged sheet (AA6111) during the DSC run has been recently discussed in detail by Lloyd et al. [2000]. In agreement with the view proposed by Lloyd et al., the absence of the peak associated with the clusters on the DSC trace for the T4
Figure 5.33 – The schematic presentation of the heat effects due to concurrent dissolution and precipitation reactions.
sample (Figure 5.22) is attributed to the clustering events during natural aging. These clusters undergo dissolution during the DSC run, giving rise to the large endothermic event, i.e. trough B. Although the peak associated with the spherical GP zones is also absent on the DSC trace for the T4 material, it may only be due to the overlap of its exothermic effect with the endothermic effect of trough B. Lloyd et al. [2000] have shown a small increase in the hardness over a temperature range close to 180°C, where the endothermic effect (trough B) is also present (see Figure 2.1), implying that spherical GP zones may form in the artificial aging of the naturally aged material. The shift of $\beta''$ peak to higher temperatures has also been attributed to the dissolution of natural aging clusters [Lloyd et al. 2000].

Based on the results of the present DSC-TEM studies (section 5.1.1.5) on the solution treated material, it is suggested that $\beta''$ and $Q'$ peaks have a considerable overlap. The shape of the DSC trace for the T4 sample suggests that this overlap is even more pronounced for the naturally aged material. The TEM observation of both lath-shape and needle-shape precipitates, i.e. $\beta''$ and $Q'$, for a T4 sample heated to the end of the peak associated with $\beta''$ formation (section 5.1.2.5), further confirms this view. Although no quantitative measurements have been done, the TEM images also suggest that $Q'$ has a relatively higher proportion than $\beta''$. Therefore, the large size of $\beta''$ peak and the small apparent size of the $Q'$ peak on the DSC trace for the T4 sample are probably due to the significant overlap between the two precipitation events. Comparing these findings with the corresponding results for the case of solution treated material, it appears that natural aging enhances the formation of $Q'$ phase. This will be discussed in detail in the following section.
Evolution of Microstructure during Aging at 180°C

The DSC and TEM results on the samples naturally aged for 2 weeks and subsequently aged for various times at 180°C are used to understand the microstructural evolution during artificial aging of the naturally aged samples. As discussed before, the absence of the first exothermic peak on the DSC traces (Figure 5.23) is related to the clustering events during natural aging.

The DSC trace for the 2-week naturally aged sample is very similar to the DSC trace for the naturally aged sheet presented by Lloyd et al. [2000], showing a very small exothermic event prior to the appearance of trough B, which is also consistent with the associated increase in hardness [Lloyd et al. 2000] (see Figure 2.1b). It is therefore possible that spherical GP zones form in the initial stages of the artificial aging of the 2-week naturally aged samples. This is also in agreement with the TEM observation of Murayama and Hono [1999], who have observed spherical GP zones in the microstructure of an Al-Mg-Si sample aged for 30 minutes at 180°C after natural aging for 70 days. Nonetheless, the TEM studies on 6111 samples, which have been artificially aged for 20 minutes at 175°C after natural aging for 30 days [Miao and Laughlin 2000b] and 30 minutes at 180°C after natural aging for 2.5 weeks [Perovic et al. 1999] have not shown any evidence of spherical GP zone formation.

Returning to the DSC traces in Figure 5.23, the reduction in the height of the peak designated as $\beta''$ for the samples aged for 30 minutes and 1 hour at 180°C seems to be due to the precipitation of both $\beta''$ and $Q'$. Although, the DSC traces show that the height of $Q'$ peak does not decrease during the first hour of aging at 180°C. The quantitative TEM result on the naturally aged sample aged for 1 hour at 180°C, shows that both $\beta''$ and $Q'$ form during this aging history (Table 5.2). Hence, the effect of $Q'$ formation is also included in the reduction of the size of the peak designated as $\beta''$. It is worth recalling that the increase in the yield strength
of a T4 sample aged for 30 minutes at 180°C is only 5 MPa. Meanwhile the size of the DSC peak for $\beta''$ has a relatively significant reduction, certainly not matching with only 5 MPa increase in the yield strength. The concept of the dissolution of the natural aging clusters during aging at 180°C, as well as the enhanced precipitation of $Q'$, provide reasonable explanation for this observation. More precisely, precipitates do form during the first 30 minutes of aging, although in smaller fractions and with higher $Q'$ proportion compared to the corresponding case of the solution treated sample, however, the reduction in the volume fraction of the natural aging clusters compensates for a significant part of hardening due to the new precipitates.

The slow rate of precipitation in the case of naturally aged samples is readily realized by comparing the DSC trace for the naturally aged sample aged for 30 minutes at 180°C with that of the similarly aged solution treated sample (Figure 5.24) as well as the quantitative TEM results. It is observed that considerably more $\beta''$ has formed in the case of the solution treated sample during 30 minutes of aging at 180°C. Although the smaller $Q'$ peak in the case of naturally aged sample may primarily be due to the overlap with $\beta''$ peak, the TEM data shows that $Q'$ formation is more favoured in the case of naturally aged samples (Table 5.2). The slow kinetics of $\beta''$ precipitation for the naturally aged samples is also evident from the TEM results. Comparing the total volume fraction of precipitates for naturally aged and solution treated samples aged for 1 hour at 180°C, (Table 5.2), it is clear that the naturally aged samples have considerably slower rate of precipitation, mainly due to the slower kinetics of $\beta''$ formation, resulting in a significantly lower volume fraction for the same time of aging at 180°C. The possible reasons for the slow rates of precipitation have been presented in section 5.2.2.1.

Comparison of the DSC traces of the naturally aged and solution treated samples for the case of 7 hour of aging at 180°C (Figure 5.25) clearly shows that $\beta''$ formation is complete after 7 hours of aging for the naturally aged sample, similar to the case of the solution treated sample.
The smaller Q' peak for the naturally aged sample implies that more Q' should have formed in this sample. This is once more in agreement with the results of TEM studies, where it shows that the volume fraction of Q' is approximately twice that for the solution treated sample aged for 7 hours at 180°C. At the same time the volume fraction of β'' is smaller than that of the solution treated sample. This results in a significant difference in the ratios of the volume fractions of β'' and Q' for the two cases, verifying that natural aging prior to artificial aging promotes Q' formation.

The characteristics of the endothermic troughs also provide information on the microstructural evolution during artificial aging of the naturally aged samples. The endothermic effects on the DSC traces for the naturally aged samples aged for 30 minutes and 1 hour at 180°C (see Figure 5.23), show similarities with the characteristics of both troughs A and B. As in the case of the solution treated samples, the small size precipitates formed during prior aging at 180°C dissolve during the DSC run when the scanning temperature reaches slightly above 180°C (i.e. similarity to trough A). On the other hand, some of the natural aging clusters may have still remained in the microstructure after aging for 30 minutes and 1 hour at 180°C. These clusters also undergo dissolution during the DSC run (i.e. similarity to trough B). This may also imply that the natural aging clusters do not dissolve very rapidly during aging at 180°C, on the contrary, their complete dissolution may take more than 1 hour at 180°C. The results of the modeling work in Chapter 6 supports this view.

The last feature to be discussed is the relative position of trough B on the DSC traces, depending on the aging history. Comparing the DSC traces for the naturally aged samples aged for 7 hour and 24 hour at 180°C (Figure 5.23), the small shift of trough B to higher temperatures indicates that the relatively larger size precipitates formed during 24 hours of aging dissolve at a slightly higher temperature range. Another interesting result arises from the comparison of the
peak-aged (7 hours at 180°C) solution treated and naturally aged samples (Figure 5.25). The slightly wider trough, shifting to higher temperatures, in the case of naturally aged sample may also imply that the precipitates are slightly larger for that case, i.e. a coarser structure. This has already been verified with TEM, where it shows that the naturally aged sample at the peak-age condition has larger precipitates while the number density of precipitates are considerably smaller than the peak-aged solution treated sample, Figure 5.34. It is also clearly observed that the naturally aged sample has a higher proportion of Q' compared to the solution treated sample.

Having obtained the above microstructural information, the smaller peak strength of the naturally aged sample, compared to that of the solution treated sample, is attributed to a coarser structure as well as a higher proportion of Q'. It is worth mentioning that a coarser structure for artificially aged samples with prior natural aging has also been reported for other Al-Mg-Si(-Cu) alloys [Pashley et al 1966, Murayama and Hono 1999, Matsuda et al. 2000]. Pashley et al. [1966] have further shown the effect of variable times of natural aging on the average length of the needle-shape precipitates after aging the solution treated and naturally aged samples for 24 hours at 160°C. Their results on a Cu-bearing alloy show that the average length slightly increases when the sample has been naturally aged for 3 hours. The average length increases appreciably by further natural aging to 3 days. For the Cu-free alloy the average length increase is similar for the samples naturally aged for 3 hours and 3 days [Pashley et al. 1966]. The effect of various natural aging times on the microstructure of AA6111, in terms of the coarseness of the microstructure and the relative proportions of $\beta''$ and Q' have not been studied.

5.3 Concluding Remarks

In this chapter, the precipitation hardening behaviour and the effect of natural aging on the structure and properties of AA6111 have been discussed. The acquired knowledge has been used to develop a process model for AA6111. The model will be presented in the next chapter.
Figure 5.34 – [001]_Al bright field TEM micrographs for (a) solution treated and (b) 2-week naturally aged samples after aging for 7 hours at 180°C. TEM observations by X. Wang.
CHAPTER 6

PROCESS MODEL

6.1 Basic Modeling Approach

The aim of the present process modeling is to combine the acquired knowledge on the processing-structure-property relationships on AA6111 with established physical principles to develop a process model for prediction of the yield strength of the alloy from the process variables of heat treatment temperatures and times:

\[ \sigma_y = f(T,t) \]  \hspace{1cm} (6.1)

More specifically, modeling of the aging processes for the solution heat-treated material and the materials with variable levels of natural aging is sought. The complete sequence of aging including underage, peak-age and overage conditions is considered. The model has been developed based on the internal state variable approach, relating the material response of interest to the microstructural variables \[ \text{[Richmond 1986, Ashby 1992, Shercliff et al.1992, Grong and Shercliff 2000]} \].

The yield strength of a precipitation hardened alloy has contributions from precipitation hardening, solid solution strengthening and the intrinsic strength of the alloy. The latter, which also includes the grain size effect, is usually minimal. The contribution from precipitation hardening to the yield stress, \( \sigma_{ppt} \), is related to the pertinent microstructural variables:

\[ \sigma_{ppt} = f_1(r, f, F, L, S) \]  \hspace{1cm} (6.2)

where \( r \) and \( f \) are the average radius and volume fraction of precipitates, respectively. \( F \) is the maximum interaction force between an average-size precipitate and the dislocation, \( L \) is the average spacing between the precipitates which are acting as obstacles to dislocation motion, and
$S$ is a microstructural variable representing the shape and orientation relationship of the precipitates with the matrix. Assuming that the shape and the orientation relationship of the hardening phases (namely $\beta''$ and $Q'$) do not change during the present aging processes, the number of variables reduces to four. Different equations can be written as follows to describe the evolution of the state variable:

\[
\frac{dr}{dt} = g_1(T,r,f) \tag{6.3}
\]

\[
\frac{df}{dt} = g_2(T,r,f) \tag{6.4}
\]

\[
\frac{dF}{dt} = g_3(T,r,f) \tag{6.5}
\]

\[
\frac{dL}{dt} = g_4(T,r,f,F) \tag{6.6}
\]

where, $T$ is temperature. Considering the above relationships, only two of these variables, namely $r$ and $f$ are required to evaluate $\sigma_{ppt}$. It is worth noting that since the model is developed for isothermal aging processes, $r$ and $f$ may also be formulated directly in integrated forms [Shercliff et al. 1992].

The contribution from solid solution strengthening to the yield stress, $\sigma_{ss}$ is a function of the concentration of the solute atoms in the matrix, $C_{ss}$:

\[
\sigma_{ss} = f(C_{ss}) \tag{6.7}
\]

$C_{ss}$ can be related to the precipitation state, due to the fact that the matrix is depleted from the solutes as the precipitation process proceeds:

\[
\frac{dC_{ss}}{dt} = g(T,r,f) \tag{6.8}
\]

After each strength component is modeled, they are assembled in the final process model by an appropriate addition rule. The process model is then calibrated with the experimental data.
In this work, information on the evolution of volume fraction during aging has been obtained using isothermal calorimetry. As discussed in Chapter 5, this method provides the total volume fraction of all types of precipitates formed during aging. Therefore, the complexity of the precipitation sequence, involving different transitional phases, is not reflected in the model.

6.2 Modeling of Yield Strength - Solution Treated Material

6.2.1 Precipitation Strengthening

Pursuing the usual approach for determining critical resolved shear stress from the interaction of gliding dislocations with point obstacles (section 2.6.1.2), the following response equation has been adopted [Gerold 1979, Ardell 1985, Lloyd 1985]:

$$\sigma_{ppt} = \frac{MF}{bL} \quad (6.9)$$

where $M$ is the Taylor factor and $b$ is the magnitude of the Burgers vector. The microstructural variables $F$ and $L$ evolve with aging time and are themselves functions of other microstructural variables as well as aging temperature. Determining the evolution laws for $F$ and $L$ during aging is, therefore, a prime task in predicting the precipitation hardening response of the material.

6.2.1.1 Average Obstacle Strength

The maximum interaction force between obstacle and dislocation, i.e. obstacle strength, is dependent on the strengthening mechanisms involved [Gerold 1979, Lloyd 1985, Ardell 1985]. The theoretical analyses show proportionality between the obstacle strength and size for most of the strengthening mechanisms when the particles are shearable [Gerold 1979, Lloyd 1985, Ardell 1985]. Most frequently, a linear relationship between the obstacle strength and size is suggested based on the theories developed for a number of strengthening mechanisms, including coherency (subjected to certain limitations), atomic order and stacking-fault
strengthening mechanisms [Hirsch and Kelly 1965, Glieter and Hornbogen 1965, Gerold and Haberkorn 1966, Gerold and Hartmann 1968, Kocks et al. 1975, Brown and Ham 1971, Melander and Persson 1978, Gerold 1979, Ardell 1985, Lee and Park 1998]. Recently, the linear relationship between $F$ and $r$ has been used for modeling of the yield strength in Al-Zn-Mg [Deschamps and Brechet 1999] and Al-Mg-Si [Myhr et al. 2001] alloys. Power-law [Nembach 1983] and logarithmic [Russell and Brown 1972] relationships between the obstacle strength and size have also been suggested for modulus strengthening mechanism. Finally, Gerold [1979] considers the assumption of a power-law relationship in general considerations. Regardless of the exact relationship, the obstacle strength increases with the obstacle size until it reaches its highest limit, i.e. $2\Gamma$, when the obstacle becomes non-shearable ($\Gamma$ is the line tension of dislocation) [Gerold 1979].

The microstructure of AA6111, as discussed in section 5.2.1.3, consists of coherent precipitates mainly $\beta''$ in the underaged condition. At the peak-aged condition $\beta''$ is the main precipitate, although both $\beta''$ and $Q'$ are present. The microstructural evolution during early stages of overaging mainly consists of the transition of $\beta''$ to $Q'$ and the coarsening of these precipitates. Direct observation of the dislocation-precipitate interaction in 6056-T6 [Vivas et al. 1997a, 1998], which has a similar composition\(^1\) as well as microstructure to AA6111, shows that these precipitates are shearable at the peak age condition. It has also been shown that the precipitates remain shearable even after extended overaging periods at the present temperature range of interest [Deschamps et al. 2000, Cheng et al. 2001]. At present, no main strengthening mechanism(s) has (have) been identified for Al-Mg-Si(-Cu) alloys. Neither, are the contributions from the individual strengthening mechanisms to the precipitation hardening known. However, considering the presence of extensive strain field surrounding $\beta''$, one can

\(^1\) Composition of AA6056 in wt\%: 0.94Si-0.87Mg-0.80Cu.
speculate that the coherency-strain strengthening is an important mechanism in the underaged and peak-aged material.

Based on the suggested relationships and the above-mentioned microstructural and mechanical behaviour information, the relationship between the average obstacle strength and the average radius in the present system is approximated by:

$$F \propto r^m$$

(6.10)

where $m = 1$ for the underaged condition and $m < 1$ for the overaged condition. As it will be shown in section 6.2.1.5 $m < 1$ is required in order to model the decrease in the yield strength for the overaging condition (when the particles are still shearable). It should also be mentioned that $r$ in the present system is the radius of an average equivalent circular cross section. In other words, for a microstructure which has important fractions of lath-shaped Q' or Q, the rectangular cross sections of the laths can be approximated by equivalent circular cross sections. The radius of an average circular cross section, including real and equivalent, is then taken as $r$. The concept introduced in equation (6.10) is schematically presented in Figure 6.1. It shows that the rate of dependence of $F$ to $r$ decreases with further increase in $r$ in the overaging regime. Finally, $F$ attains the highest limit of $2\Gamma$ when the precipitates become non-shearable (Orowan mechanism).

In order to estimate $F$, a normalized form of relationship (6.10) is used:

For $r \leq r_{\text{peak}}$:

$$m = 1 \quad \text{and} \quad F = \frac{r}{r_{\text{peak}}} F_{\text{peak}}$$

(6.11)

For $r_{\text{peak}} \leq r \leq r_c$:

$$m < 1 \quad \text{and} \quad F = \left(\frac{r}{r_{\text{peak}}}\right)^m F_{\text{peak}}$$

(6.12)
Figure 6.1 – A schematic presentation of the variation of $F$ with $r$. 

$F$

$2\Gamma$

$F_{peak}$

$r_{peak}$  $r_c$  $r$
where $r_{\text{peak}}$ and $F_{\text{peak}}$ are the average radius and the average obstacle strength at the peak age condition and $r_c$ is the average radius of precipitates at the shearable to non-shearable transition. When the precipitates become non-shearable the maximum interaction force between obstacle and precipitate is constant, i.e. when $r \geq r_c$:

$$F = 2\Gamma$$  \hspace{1cm} (6.13)

The suitability of relationship (6.11) has been verified using the experimental data in section 6.2.4.1. Equation (6.12) has also given satisfactory results for $r = r_{\text{peak}}$ and $r = r_c$ (see section 6.2.4.2).

### 6.2.1.2 Average Obstacle Spacing

The average obstacle spacing can be determined in accordance with the assumptions for the relative obstacle strength. Using the breaking angle as the measure for the strength of obstacles, according to Brown and Ham [1971], for cases where $\phi_c \leq 100^\circ$ the obstacles are considered “strong”, whereas for $\phi_c \geq 100^\circ$ the obstacles are regarded “weak”. The highest and the lowest limits of breaking angles for strong and weak obstacles, respectively, can be slightly modified from the above limit given by Brown and Ham. It is first recalled from Chapter 2 that the relationship derived for the critical stress based on Friedel statistics (equation 2.15 or 2.16) is valid for large breaking angles [Brown and Ham 1971, Ardell 1985, Lloyd 1985]. In addition, to satisfy the geometry of the unzipping process, according to which the Friedel relationship has been derived, $\phi_c$ must be larger than 120° [Brown and Ham 1971, Ardell 1985]. It has further been shown [Brown and Ham 1971, Ardell 1985, Lloyd 1985] that the predictions based on Friedel statistics are in good agreement with the results of the computer simulation studies [Forman and Makin 1966, Hanson and Morris 1975] for breaking angles larger than 120°/140°. In the case of strong obstacles, a close examination of Figure 2.7 shows that the relationship
suggested by Brown and Ham [1971] gives accurate results for $0 \leq \varphi_c \leq 120^\circ$, as also stated by Ardell [1985]. Based on the above information, the following definitions are adopted for weak and strong obstacles:

Weak obstacles: $\varphi_c > 120^\circ$

Strong obstacles: $\varphi_c < 120^\circ$

*Strong Obstacles*

The effective spacing between strong obstacles is estimated based on the planar center-to-center distance between them. As clearly shown by Kelly [1972], the number of particles that intersect the slip plane is influenced by the shape of the precipitates, being larger for elongated precipitates when compared to spherical particles. Consequently, the average obstacle spacing for elongated precipitates becomes smaller than the average spacing for the spherical precipitates with the same volume fraction and volume per precipitate [Kelly 1972, Gerold 1979]. Nie et al. [1996] have further shown that rod-shaped precipitates aligned in the $<100>$ directions of the aluminum matrix are more effective, in raising the number density of particles that intersect the slip plane, than the randomly oriented rods. In the present case $\beta''$ and $Q'$ phases are both elongated precipitates aligned parallel to the $<100>$ directions of the matrix. Therefore, the average obstacle spacing is estimated by taking into account their shape and orientation relationship with the matrix. Considering that $\beta''$ is the major hardening precipitate in this system, the following estimation of the obstacle spacing is based on the needle-shaped precipitates (i.e. circular cross section). However, it can generally include the cases for which the relative volume fraction of the lath-shaped $Q'$ (or $Q$) is also significant. For these cases, as stated earlier, the average rectangular cross section of the laths can be approximated by an equivalent circular cross section.
Considering the orientation relationship between the needle-shape obstacles along \(\langle 100\rangle\) and the \(\{111\}\) planes of matrix, we can find the shortest spacing, \(L\), between obstacles. Figure 6.2(a) shows the relative positions of three needle-shape precipitates which interact with the slip plane. This kind of arrangement results in a triangular array of obstacles on the glide plane.

The number of precipitates per unit area of slip plane, \(N_A\), can be obtained using the reference triangle ABC on the triangular array of precipitates, Figure 6.3(a):

\[
N_A = \frac{n_a}{A} \tag{6.14}
\]

where \(n_a\) is the number of precipitates in the reference triangle and \(A\) is the area of the triangle.

As it is shown in Figure 6.3(a), approximately \(\frac{1}{6}\) of each of three precipitates belong to the triangle:

\[
n_a = 3 \times \frac{1}{6} = \frac{1}{2} \tag{6.15}
\]

Using Figure 6.3(b):

\[
A = \frac{L \cdot h}{2} = \frac{L \cdot L \cos(30^\circ)}{2} = \frac{\sqrt{3}}{4} L^2 \tag{6.16}
\]

Therefore,

\[
N_A = \frac{1/2}{\frac{\sqrt{3}}{4} L^2} = \frac{2}{\sqrt{3} L^2} \tag{6.17}
\]

Or,

\[
L = \sqrt{\frac{2}{\sqrt{3} N_A}} \tag{6.18}
\]

Since it is usually convenient to relate \(L\) to the volume fraction of precipitates, it will be useful to find the relationship between \(N_A\) and volume fraction, \(f\). According to Fullman [1953]:

\[
N_A = P \cdot N_v \tag{6.19}
\]
Figure 6.2 – (a) Orientation relationship between needle-shape precipitates and a \{111\} plane of matrix. (b) Dislocation-obstacle interaction in a triangular array of obstacles.

Figure 6.3 – (a) Triangular array of precipitates on a \{111\} plane. (b) Reference triangle ABC.
where, $P$ is the probability that a needle shape precipitate oriented along $<100>$ intersects a \{111\} plane and $N_V$ is the number of precipitates per unit volume. Considering $\alpha$ to be the angle between $<111>$ and $<100>$, which the former is the direction perpendicular to \{111\}, $P$ can be estimated as follows:

\begin{equation}
P = \frac{l \cos \alpha}{1}
\end{equation}

(6.20)

Also, for precipitates with the average radius of $r$ and the average length of $l$, $N_V$ is related to $f$ as follows:

\begin{equation}
N_V = \frac{f}{\pi r^2 l}
\end{equation}

(6.21)

Replacing (6.20) and (6.21) in (6.19):

\begin{equation}
N_A = \frac{f}{\sqrt{3} \pi r^2}
\end{equation}

(6.22)

Finally replacing for $N_A$ in equation (6.18) the following relationship between $L$ and $f$ is obtained:

\begin{equation}
L = \left(\frac{2\pi}{f}\right)^{1/2} r
\end{equation}

(6.23)

Equation (6.23) has also been derived by Nie et al. [1996], although the details of the two derivations are slightly different. It should be added that, similar to the findings in the case of random array of strong obstacles [Kocks 1966a, 1966b & 1967, Forman and Makin 1966], the effective spacing in the present case may be slightly larger than the shortest obstacle spacing as derived in equation (6.23). The effective spacing, on the other hand, is reduced due to the finite size of the obstacles [Brown and Ham 1971, Nie et al. 1996]. Therefore, it can be reasonably supposed that the two opposite effects cancel out, and equation (6.23) provides a fair estimation of the effective obstacle spacing.
Weak Obstacles

In the case of weak obstacles, the effective obstacle spacing, \( L_F \), is derived by using Friedel statistics [Friedel 1962, Fleischer and Hibbard 1963, Brown and Ham 1971, Ardell 1985, Lloyd 1985]. For a regular array of \( N_A \) obstacles per unit area the relationship between \( L_F \) and \( \varphi_e \) (i.e. equation 2.13) can be re-written as:

\[
L_F = \left[ N_A \cos\left(\frac{\varphi_e}{2}\right) \right]^{-1/2} \tag{6.24}
\]

In the above relationship, \( \cos\left(\frac{\varphi_e}{2}\right) \) can be obtained by using the force balance on the obstacle (see Figure 2.5):

\[
\cos\left(\frac{\varphi_e}{2}\right) = \frac{F}{2\Gamma} \tag{6.25}
\]

Using equations (6.17), (6.24) and (6.25), \( L_F \) is derived as:

\[
L_F = \left( \frac{\sqrt{3}\Gamma}{F} \right)^{1/2} L \tag{6.26}
\]

Replacing equation (6.23) in (6.26), \( L_F \) is obtained as a function of \( f, r \) and \( F \):

\[
L_F = \left( \frac{2\sqrt{3}\pi}{Ff} \right)^{1/2} r \tag{6.27}
\]

Using equations (6.26) and (6.25), it can be found that for \( \frac{\varphi_e}{2} = 30^\circ \) (or \( \varphi_e = 60^\circ \)) \( L_F \) is equal to \( L \). In other words, for cases where \( \varphi_e < 60^\circ \), equation (6.26)/(6.27) will give the obstacle spacing incorrectly smaller than the shortest possible spacing for the triangular array and therefore will significantly overestimate the yield strength. This has also been shown by Brown and Ham [1971].
6.2.1.3 Estimation of Volume Fraction

Assuming that precipitation in AA6111 is a nucleation and growth process, the Johnson-Mehl, Avrami, Kolomokorov (JMAK) model [Johnson and Mehl 1939, Avrami 1939, 1940 & 1941, Kolmogorov 1937] is adapted to describe the precipitation kinetics:

\[ f_r = 1 - \exp(-kt^n) \]  \hspace{1cm} (6.28)

where \( f_r \) is the relative volume fraction of precipitates, or alternatively described, the fraction transformed at time \( t \). Assuming that the precipitation process is complete at the peak-age condition, \( f_r \) can be defined as:

\[ f_r = \frac{f}{f_{\text{peak}}} \]  \hspace{1cm} (6.29)

where \( f_{\text{peak}} \) is the volume fraction of the precipitates at the peak-age condition. The JMAK parameters, \( k \) and \( n \) can be obtained by the usual procedure of plotting the \( \ln \ln \left( \frac{1}{1-f_r} \right) \) values vs. \( \ln t \) and finding the intercept and slope of the resultant line, according to:

\[ \ln \ln \left( \frac{1}{1-f_r} \right) = \ln k + n \ln t \]  \hspace{1cm} (6.30)

The value of \( f_r \) can be related to the heat evolution due to precipitation during isothermal calorimetry, \( \frac{dQ}{dt} \), as shown in section 5.1.1.3 [see also Smith 1994, 1997, 1998a, Starink and Zahra 1999]. As the time to the peak age, \( t_{\text{peak}} \), for the present temperature range of interest, corresponds to the completion of the heat evolution during isothermal calorimetry, i.e. \( t_f \), equation (5.4) can be re-written as follows:

\[ f_r = \frac{\int_{t_{\text{peak}}}^{t_f} \frac{dQ}{dt} \, dt}{\int_{t_{\text{peak}}}^{t_f} \frac{dQ}{dt} \, dt} = \frac{\int_{t_{\text{peak}}}^{t_f} \frac{dQ}{dt} \, dt}{A_{\text{opt}}} \]  \hspace{1cm} (6.31)
Considering the isothermal calorimetry experiments and recalling that the calorimeter is unstable for the first 7-10 minutes of the experiment, the zero time should be shifted to \( t_0 \) before the fitting procedure:

\[
t = t_{\text{exp}} - t_0
\]  

(6.32)

where \( t_{\text{exp}} \) is the actual time recorded by the calorimeter and \( t_0 \), as shown in Figure 5.7(b), is the time when the exothermic event starts to emerge. After applying the time shift, the evolution of \( f_r \) is estimated according to equation (6.31). The estimated values for \( f_r \) are then used to evaluate \( \ln \ln \left( \frac{1}{1 - f_r} \right) \) and subsequently plot them vs. \( \ln t \), Figure 6.4. The linear approximations, according to equation (6.30), are obtained for the \( f_r \) range of 5%-95%, as shown in Figure 6.4. It is noticed that the slopes of the lines, i.e. \( n \), are approximately unity for all aging temperatures.

Having known that the size of \( \beta'' \) (as well as \( Q' \)) increases during aging at 180°C (see Table 5.2), the \( n = 1 \) result is consistent with the predictions of the kinetic theories for the diffusion-controlled growth of needle-shape/lath-shape precipitates [Christian 1975, Doherty 1996].

Figure 6.5 shows the isothermal calorimetry traces along with the JMAK model fitted according to the values obtained for \( k \) and \( n \). It is shown that although the fits are not exact, they represent the experimental data reasonably well. The good agreement between the JMAK model and the experiment is also illustrated in Figure 6.6, where the evolution of \( f_r \) obtained through the model is compared with the values acquired directly from integrating the calorimetry traces, i.e. equation 6.31.

Having determined \( n \) and \( k \) at various temperatures, the next step is to determine the temperature dependence of \( k \). The rate constant \( k \) has an Arrhenius type relationship with temperature:
Figure 6.4 - Plots of $\ln \ln \left(\frac{1}{1-f_r}\right)$ vs. $\ln t$ for the $f_r$ range of 5% - 95%.
Figure 6.5 – The isothermal calorimetry traces are simulated by the JMAK kinetics model. (Different Y-axes are used to show the fit clearly. The data for different temperatures have been compared in Figure 5.7)
Figure 6.6 – Comparison of the relative volume fractions obtained using the JMAK model with the values acquired directly from integrating the calorimetry traces.
\[ k = k_0 \exp(-Q/RT) \]  \hspace{1cm} (6.33)

where \( k_0, Q \) and \( R \) are the proportionality constant, apparent activation energy and the universal gas constant, respectively. Figure 6.7 shows the Arrhenius type plot for \( k \), which results in an activation energy of 58 (± 5) kJ/mole \( (k_0 = 3280 \text{s}^{-1} \text{ for } Q = 58 \text{ kJ/mole}) \). This activation energy should not be regarded as the activation energy for the precipitation process. As discussed by Berkenpas et al. [1986] and Luo et al. [1992], the apparent activation energy obtained from the slope of the plot of \( \ln(k) \) vs. \( 1/T \) is the sum of the positive and apparent negative energy values for the nucleation and diffusional growth mechanisms. Thus resulting from a combination of effects, it does not have a physical meaning by itself.

### 6.2.1.4 Estimation of \( \sigma_{ppt} \) for Underage and Peak-age Conditions

The estimates for \( \sigma_{ppt} \) can be obtained by replacing the corresponding relationships for \( F \) and \( L \) in equation (6.9). To proceed, both cases of strong and weak obstacles will be considered.

**Strong Obstacles**

Replacing equations (6.11), (6.23) and (6.29) in equation (6.9):

\[
\sigma_{ppt} = \frac{M \frac{r}{r_{peak}} F_{peak}}{b \left( \frac{2\pi}{f} \right)^{1/2} r} = \frac{MF_{peak}}{br_{peak} (2\pi)^{1/2} f^{1/2}} f^{1/2} = C_1 f^{1/2}
\]  \hspace{1cm} (6.34)

Therefore, \( \sigma_{ppt} \) is dependent only on the volume fraction of precipitates. This result is similar to the relationship derived for the maximum critical resolved shear stress due to coherency strengthening in the case of coherent spherical precipitates [Ardell 1985], order strengthening for
Figure (6.7) – JMAK constant $k$ shows an Arrhenius relationship with temperature.
strong obstacles [Ardell 1985] as well as modulus strengthening formulation proposed by Cartaud et al. [1976] (see Table 2.2).

Weak Obstacles

Replacing equation (6.27) in equation (6.9):

$$\sigma_{ppt} = \frac{MF^{3/2} f^{1/2}}{b(2\sqrt{3\pi})^{1/2} \Gamma^{1/2} r}$$  \hspace{1cm} (6.35)

Now using equations (6.11) and (6.29):

$$\sigma_{ppt} = \frac{MF_{\text{peak}}^{3/2} f_{\text{peak}}^{1/2}}{b(2\sqrt{3\pi})^{1/2} \Gamma_{\text{peak}}^{1/2} r_{\text{peak}}^{3/2}} r^{1/2} f^{1/2} = C_2 r^{1/2} f_{r}^{1/2}$$  \hspace{1cm} (6.36)

Therefore, for the case of weak obstacles, $\sigma_{ppt}$ is dependent on both $r$ and $f$. This result is in agreement with the predictions of the theoretical analysis for the coherency strengthening mechanism for small coherent precipitates, as well as the atomic order (for small or weak obstacles) and stalking fault strengthening mechanisms (see Table 2.1) [Brown and Ham 1971, Ardell 1985, Embury et al. 1989].

6.2.1.5 Estimation of $\sigma_{ppt}$ for Overaging Condition

The volume fraction of precipitates is assumed to be constant during overaging. Hence:

$$f = f_{\text{peak}}$$  \hspace{1cm} (6.37)

Below, $\sigma_{ppt}$ is formulated according to the extent of overaging. For $r_{\text{peak}} \leq r \leq r_c$ both cases of strong and weak obstacles are considered. It is obvious that the obstacles are strong for $r > r_c$, i.e. when the precipitates are non-shearable.
\( r_{\text{peak}} \leq r \leq r_c: \)

**Strong Obstacles**

Replacing equations (6.12), (6.23) and (6.37) in equation (6.9):

\[
\sigma_{\text{ppt}} = \frac{M \left( \frac{r}{r_{\text{peak}}} \right)^m F_{\text{peak}}}{b \left( \frac{2\pi}{f_{\text{peak}}} \right)^{1/2} r} = \frac{MF_{\text{peak}} f_{\text{peak}}^{1/2}}{b(2\pi)^{1/2} r_{\text{peak}}^{m-1}} = C_4 r^{m-1} \tag{6.38}
\]

It is worth emphasizing here that the yield strength decreases when \( m < 1 \).

**Weak Obstacles**

Replacing equations (6.12), (6.27) and (6.37) in equation (6.9):

\[
\sigma_{\text{ppt}} = \frac{M \left[ \left( \frac{r}{r_{\text{peak}}} \right)^m F_{\text{peak}} \right]^{3/2} f_{\text{peak}}^{1/2}}{b(2\sqrt{3}\pi)^{1/2} \Gamma^{1/2} r} = C_4 r^{(\frac{2m}{3})-1} \tag{6.39}
\]

Equation (6.39) implies that if \( m > \frac{2}{3} \), \( \sigma_{\text{ppt}} \) will increase with particle size for constant \( f \) (consistent with the comments of Gerold [1979]). In the present case, considering the results discussed in Chapter 5, \( f \) can be assumed as constant (i.e. equation 6.37 is a reasonable approximation). Therefore, it is expected from equation (6.39), that either \( m < \frac{2}{3} \) or the obstacles are not weak (i.e. the weak obstacle model does not apply for the overaging condition).

\( r \geq r_c \)

Obstacles with \( r \geq r_c \) are non-shearable and hence are considered strong. Replacing equation (6.13), (6.23) and (6.37) in equation (6.9):
\[ \sigma_{ppl} = \frac{2MT}{b(\frac{2\pi}{f_{peak}})^{1/2}} = \frac{MTf_{peak}^{1/2}}{b(\pi/2)^{1/2}}r^{-1} = C_3r^{-1} \] (6.40)

It is clear that the only variable needed to estimate \( \sigma_{ppl} \) in all the above cases is \( r \). For the present modeling purposes, the reduction in the yield strength beyond the peak-age condition is assumed to be due to the coarsening. Therefore, a coarsening law can be utilized to estimate \( r \) during overaging. Accordingly, LSW [Lifshitz and Slyozov 1961, Wagner 1961] theory for coarsening is adapted to estimate \( r \) beyond the peak strength:

\[ r^3 - r_{\text{peak}}^3 = k(t - t_{\text{peak}}) \] (6.41)

The rate constant \( k \) is given by [Ardell 1969, Porter and Easterling 1981]:

\[ k = \frac{2\gamma Dc_e V_m^2}{\xi^3 RT} \] (6.42)

where \( \gamma \) is the interfacial energy of the precipitate/matrix interface, \( D \), is the diffusion coefficient of the solute in the matrix, \( c_e \) is the concentration of solute in equilibrium with a particle of infinite size (i.e. the solubility limit), \( V_m \) is the molar volume of the precipitate and \( \xi \) is a constant factor related to the size distribution of precipitates. Having known that both \( D \) and \( c_e \) increase exponentially with temperature [Porter and Easterling 1981], and assuming that \( \gamma, V_m, \) and \( \xi \) are all constant during overaging, equation (6.42) can be written as:

\[ k \propto \frac{Dc_e}{T} \] (6.43)

Or,

\[ k = \frac{A}{T} \exp(-Q_A / RT) \] (6.44)

where \( A \) is a constant factor and \( Q_A \) is an apparent activation energy. Equation (6.44) can be re-written as:
\[ kT = A \exp(-Q_A / RT) \] \hspace{1cm} (6.45)

The evolution of \( r \) during overaging will be obtained by using equations (6.41) and (6.45) and the calibration of the model to the experimental tensile data (see section 6.2.4.2).

6.2.2 Solid Solution Strengthening

The contribution from solid solution strengthening to the yield stress is given approximately by [Nabarro 1967, Labausch 1970, Shercliff and Ashby 1990]:

\[ \sigma_{ss} = a \bar{C}_t^{2/3} \] \hspace{1cm} (6.46)

where \( a \) is a constant related to the properties of the solute and \( \bar{C}_t \) is the average solute concentration in the matrix at aging time \( t \). Assuming a quasi-binary system, the concentration of solutes in the matrix, on the other hand, is related to the volume fraction of the precipitates, as the solutes are depleted from the matrix by the precipitation process. According to Shercliff and Ashby [1990]:

\[ f_r = \frac{C_i - \bar{C}_t}{C_i - C_e} \] \hspace{1cm} (6.47)

where \( C_i \) is the initial solute concentration and \( C_e \) is the solute concentration at equilibrium at the aging temperature. In the present case, \( C_e \) can be considered as the solute concentration at the peak age condition, where \( f_r \) is assumed to be unity. It is further assumed that when \( f \) approaches unity, the matrix tends to become depleted of all its solutes, i.e. \( C_e = 0 \). Thus, equation (6.47) can be written as:

\[ f_r = 1 - \frac{\bar{C}_t}{C_i} \] \hspace{1cm} (6.48)

Re-arranging equation (6.48) and replacing it in (6.46), gives:
\[ \sigma_{ss} = a[C_i(1-f_r)]^{2/3} = aC_i^{2/3}(1-f_r)^{2/3} = b(1-f_r)^{2/3} \] (6.49)

Therefore, when \( f_r = 1 \), \( \sigma_{ss} \) becomes zero. The constant \( b \) has the units of stress, and is obtained by considering the initial condition, i.e. \( f_r = 0 \). If \( \sigma_{0ss} \) is designated for \( \sigma_{ss} \) at \( t = 0 \), then:

\[ b = \sigma_{0ss} \] (6.50)

and therefore,

\[ \sigma_{ss} = \sigma_{0ss}(1-f_r)^{2/3} \] (6.51)

where \( \sigma_{0ss} \) is the contribution of solid solution strengthening to yield strength for the as-quenched material.

### 6.2.3 Overall Strength

The overall strength of the artificially aged alloy has contributions from the precipitates, the solid solution and the intrinsic strength of aluminum (the grain size effect is negligible for this alloy system [Burger et al. 1995]). Resembling the mixture of a few strong and many weak obstacles, a linear addition is the appropriate addition rule for the contributions from precipitates and solute atoms [Ardell 1985, Brown and Ham 1971]. The contribution from the pure matrix, \( \sigma_i \), is also added linearly [Ardell 1985, Lloyd 1985].

\[ \sigma_y = \sigma_{ppt} + \sigma_{ss} + \sigma_i \] (6.52)

### 6.2.4 Calibration of the Model

It is assumed that the peak-age values for \( r, f \) and \( F \) are independent of temperature in the temperature range of 160-220°C. The assumption for constant \( f \) is supported by the results of the isothermal calorimetry experiments, as discussed in section 5.2.1.3. The unknown parameters
needed to predict the yield strength should be calibrated by using data from the aging curves as well as the literature:

\[ \sigma_i = 10 \text{ MPa} \] for pure Al, [Deschamps and Brechet, 1999]

\[ \sigma_y = 60 \text{ MPa} \] for the as-quenched material (experimental)

Since \( \sigma_y \) for the as-quenched material has no contribution from precipitation, then according to equation (6.52):

\[ \sigma_{0ss} = \sigma_y - \sigma_i = 50 \text{ MPa} \]

### 6.2.4.1 Underage and Peak-age Condition

The experimental results have shown that the peak yield strength can be considered as constant (~335 MPa) in the range of temperatures between 140°C and 220°C. Therefore, at the peak age condition:

\[ \sigma_{ppt} = 335 - 10 = 325 \text{ MPa} \]

It has also been assumed that at the peak-age:

\[ f_r = 1 \]

Using the TEM result for the cross sectional area of \( \beta'' \) at the peak (see Table 5.2):

\[ r_{peak} = 1.75 \text{ nm} \]

\( C_1 \) and \( C_2 \) (for strong and weak obstacle models, respectively) are estimated as follows:

According to the reduced form of equation (6.34):

\[ C_1 = \frac{\sigma_{ppt}}{f_r^{1/2}} = 325 \text{ MPa} \]

According to the reduced form of equation (6.36):

\[ C_2 = \frac{\sigma_{ppt}}{r^{1/2} f_r^{3/2}} = 7.77 \times 10^{12} \text{ Nm}^{-5/2} \]
Estimation of the Obstacle Strength

The experimental data for aging at 180°C has been used for estimation of $F$, using both strong and weak obstacle models. The following procedure has been used:

1. For strong obstacle model, equation (6.23) is replaced in equation (6.9) and re-arranged:

$$ F = \frac{\sigma_{ppt} b (2\pi)^{1/2} r}{M f} \quad (6.53) $$

2. For weak obstacle model, equations (6.27) is replaced in equation (6.9) and re-arranged:

$$ F = \left[ \frac{b (2\sqrt{3\pi})^{1/2} \Gamma^{-1/2} r \sigma_{ppt}}{M f^{1/2}} \right]^{2/3} \quad (6.54) $$

3. The values for $r$ are obtained using the TEM data for the cross sectional area of $\beta''$ (see Table 5.2).

4. Using the TEM result for $f_{peak}$ and the isothermal calorimetry data for $f_r$, the volume fraction values, $f$, for above aging times are calculated. The reason that the $f_r$ values obtained from TEM are not used is that those $f_r$ values for short aging times (i.e. 15 minutes and 30 minutes) do not reflect the contributions from the spherical GP zones (see Table 5.3 and section 5.2.1.3). In contrast, the $f_r$ values obtained by isothermal calorimetry reflect the contributions from all precipitates for the entire underaging period. Therefore, the correct values for $f$ are found by the products of $f_r$, obtained from isothermal calorimetry, and $f_{peak}$ from TEM.

5. Using the yield strength data and the isothermal calorimetry data for $f_r$, $\sigma_{ppt}$ is estimated according to equations (6.51) and (6.52).

6. Using equations (6.53) and (6.54) and the experimental data, as mentioned above, the evolution of $F$ during aging for both strong and weak obstacles are estimated, Table 6.1.
Table 6.1 – Evolution of $F$, $\varphi_c$ and $\frac{F}{r}$ during underaging.

<table>
<thead>
<tr>
<th>Aging time at 180°C (hr)</th>
<th>$f_r$</th>
<th>$r$ (nm)</th>
<th>$F$ (nN)</th>
<th>$\frac{F}{r}$ (N/m)</th>
<th>$\varphi_c$ (°)</th>
<th>$F$ (nN)</th>
<th>$\frac{F}{r}$ (N/m)</th>
<th>$\varphi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.59</td>
<td>1.21</td>
<td>0.95</td>
<td>0.79</td>
<td>120</td>
<td>1.20</td>
<td>0.99</td>
<td>116</td>
</tr>
<tr>
<td>0.5</td>
<td>0.77</td>
<td>1.19</td>
<td>0.97</td>
<td>0.82</td>
<td>121</td>
<td>1.22</td>
<td>1.02</td>
<td>117</td>
</tr>
<tr>
<td>1</td>
<td>0.89</td>
<td>1.27</td>
<td>1.09</td>
<td>0.85</td>
<td>116</td>
<td>1.31</td>
<td>1.03</td>
<td>112</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1.75</td>
<td>1.60</td>
<td>0.91</td>
<td>87</td>
<td>1.70</td>
<td>0.97</td>
<td>79</td>
</tr>
</tbody>
</table>
As it is noticed, the values of $F$ estimated through weak obstacle model are slightly larger than the corresponding values for strong obstacle model. This result is expected for the breaking angles larger than $60^\circ$ (see section 6.2.1.2) where $L_F$ is larger than $L$ (i.e. for the same $\sigma_{pl}$, $F$ should be larger for the weak obstacle case). The values obtained for $F$ at the peak-age condition (i.e. 7 hours at $180^\circ$C), according to both strong and weak obstacle models, are different from the value reported by [Vivas et al. 1997a] for AA6056-T6 (i.e. 0.6 nN). However, the values estimated in the present work and the one reported for AA6056-T6 are all less than $2\Gamma$ (assuming constant line tension, $2\Gamma = Gb^2 \approx 2.2$ nN).

It is of interest now to examine the relationship between the estimated values for $F$ and the experimental values for $r$ for both weak and strong obstacles. As shown in Table 6.1, the $\frac{F}{r}$ values are almost constant for both cases of strong and weak obstacles and hence the proposed linear relationship between $F$ and $r$ is verified.

**Estimation of the Evolution of the Dislocation Breaking Angle**

The evolution of the dislocation breaking angle, i.e. $\varphi_c$, during aging can be estimated by equating equations (2.8) and (6.11) and solving for $\varphi_c$:

$$F = 2\Gamma \cos \left( \frac{\varphi_c}{2} \right) = \frac{r}{r_{peak}} F_{peak} \Rightarrow \frac{\varphi_c}{2} = \cos^{-1} \left( \frac{F_{peak}}{2\Gamma r_{peak}} \right)$$

(6.55)

The values obtained for $\varphi_c$ according to the estimated values for $F_{peak}$ for both cases of strong and weak obstacles are listed in Table 6.1. It is noticed that the breaking angles estimated through both strong and weak obstacle models are approximately $120^\circ$ for 15 minutes and 30 minutes of aging at $180^\circ$C. The breaking angles become smaller by further aging. For the peak-
age condition $\varphi_c$ is in the range of 80-90°. Hence, for early stages of aging, when $r$ is approximately 1.2 nm, the obstacles may be considered in either strong or weak obstacle categories. For later stages of aging, when $r$ is relatively larger, the obstacles are strong (e.g. peak-age condition).

### 6.2.4.2 Overage Condition

First the apparent radius of the precipitates at the shearable to non-shearable transition, i.e. $r_c$, should be determined. The term “apparent radius” is used here to emphasize that the microstructure at the shearable to non-shearable transition probably consists of mainly Q’ (and/or Q) phase, which has a rectangular cross section. Hence, the radius obtained below can be considered as the radius of a circular cross section with the same average cross sectional area as Q’ (and/or Q).

It is suggested that the shearable to non-shearable transition in the present alloy occurs at a yield strength range of 260-270 MPa during overaging [Cheng et al. 2001]. Therefore, using equation (6.40) $r_c$ can be obtained:

$$\sigma_{ppt} = 265 - 10 = 255 \text{ MPa}$$

$$\Gamma = \frac{1}{2} G b^2, (G = 27 \text{ GPa})$$

$$r_c = \frac{2 M \Gamma}{b \left( \frac{2\pi}{f_{\text{peak}}} \right)^{1/2} \sigma_{ppt}} \approx 3.1 \text{ nm}$$

Now to find $C_3$ and $m$, equation (6.38) is applied for both the peak-age condition (where $r_{\text{peak}}$ and $\sigma_{ppt}$ are known) and the point of shearable to non-shearable transition (where $r_c$ and $\sigma_{ppt}$ are estimated), and the resulting equations are solved for the two unknown parameters. The
results are:

\[ m \equiv 0.6 \]

and

\[ C_3 = 102120 \text{ Nm}^{-1.6} \]

Since the obstacles are estimated to be strong for the peak-age condition (and hence beyond the peak) \( C_4 \) is not needed to be calibrated. For the non-shearable precipitates \( C_5 \) is obtained by replacing the values for \( \sigma_{ppt} \) and \( r \) at the shearable to non-shearable transition in equation (6.40):

\[ C_5 = 0.8 \text{ Nm}^{-1} \]

**Estimation of the Evolution of \( r \) during Coarsening**

Since, no independent data for the evolution of \( r \) during overaging is available, the following procedure is used to back calculate \( r \) from the experimental tensile data at 180°C, 200°C and 220°C. It should be mentioned that the strong obstacle model, i.e. equation (6.38) is used for this procedure (as shown in Table 6.1, the obstacles are suggested to be strong at the peak-age condition, and by corollary during overaging, for the present alloy).

Using equation (6.52) and according to the assumption that \( \sigma_{ss} = 0 \) during overaging:

\[ \sigma_{ppt} = \sigma_y - 10 \text{ MPa} \]

Using the above relationship and replacing the experimental data for \( \sigma_y \), a set of data for \( \sigma_{ppt} \) is obtained at each aging temperature. Then, replacing for \( \sigma_{ppt} \) and \( C_3 \) in equation (6.38), the corresponding set of values for \( r \) is found.

In order to examine the applicability of equation (6.41) to the evolution of \( r \) (i.e. back calculated \( r \)) during overaging, \( r^3 \) is plotted versus \(( t - t_{peak} )\) for the above three aging
temperatures. Figure 6.8(a)-(c) shows these plots along with their linear fits. It is noticed that at each case the linear fits closely approximate the data points, i.e. $R^2 > 0.96$. According to equation (6.41), the slopes of the lines fitted to the above plots are the values for $k$ at each temperature. The kinetics of coarsening can then be determined according to equation (6.45) by plotting $kT$ vs. $1/T$. The slope of the line fitted to the above plot, as shown in Figure 6.8(d), provides the kinetic parameters of $A$ and $Q_A$:

$$A = 8.0 \times 10^{-7} \text{ m}^3 \text{s}^{-1} \text{K}$$

$$Q_A = 205 \text{ kJ/mole}$$

Having determined $A$ and $Q_A$, $k$ is obtained through equation (6.44). Consequently, the evolution of $r$ during overaging can be found through equation (6.41). It should be noticed, however, that the kinetics of coarsening for very long aging periods may differ from the one determined as above, due to the phase transitions involved concurrent with the coarsening process.

As a result of the above calculations, an estimate for the apparent solvus enthalpy can be given by considering that according to equations (6.43) and (6.44) $Q_A$ is the summation of the energy terms from diffusion and solubility limit. Hence, considering that the activation energy for diffusion of the solutes in this system is approximately 120-140 kJ/mole [Hatch 1984, Lloyd 1998], the apparent solvus enthalpy is estimated to be in the range of 65-85 kJ/mole. It is worth mentioning that the apparent solvus boundary for this condition of overaging comprise probably of both $\beta''$ and $Q'$ (see section 5.2.1.3).

### 6.2.5 Model Implementation

The model has been implemented in a spreadsheet program.
Figure 6.8 – The back-calculated $r$ from the tensile data is used to find the temperature dependence of $r$ for the overaging regime. (a), (b) and (c) $r^3$ vs. coarsening time, (d) Arrhenius-type plot for $kT$. 

180°C

220°C

200°C

$Q_A=205$ kJ/mole
6.2.5.1 Strong Obstacle Model

Figure 6.9 shows the modeling results for the strong obstacle assumption along with the experimental data for the aging processes at 180°C, 200°C and 220°C. It is observed that the modeling results have very good agreements with the experimental data in the entire aging period.

6.2.5.2 Validation of the Strong Obstacle Model

The validity of the model is verified by comparing the model predictions with the independent experimental data for aging at 160°C. Figure 6.10 demonstrates the good agreement between the model predictions and the experimental results.

6.2.5.3 Weak Obstacle Model

The model based on the weak obstacle assumption has been examined for the aging process at 180°C, for which direct experimental data for the evolution of $r$ is available. Figure 6.11 compares the results of the weak obstacle model with the experimental data as well as the results of the strong obstacle model. For a more decisive comparison and in order to avoid the errors from the fitting procedures, the values of $f_r$ and $r$ which are used in Figure 6.11(a), have been taken directly from the experimental data (for the aging times of 15 minutes, 30 minutes and 1 hour). It is noticed that the weak obstacle model closely approximates the experiment in the early stages of aging (i.e. 15 minutes at 180°C), surpassing the strong obstacle model. However, the agreement between the model and the experimental data declines as the aging proceeds to later stages. The reverse is true for the strong obstacle model.
Figure 6.9 – Comparison of modeling results, using the strong obstacle assumption, and the experimental data for the yield strength of solution heat treated material aged at 180°C, 200°C and 220°C.
Figure 6.10 – Comparison of the model predictions and the experimental results for aging at 160°C.
Figure 6.11 – Comparison of the results of the weak and strong obstacle models and the experimental data for the solution treated material, aged at 180°C. The model calculations are based on (a) the experimental values for $f_r$ and $r$ and (b) the fitted values for $f_r$ and $r$. For better clarity the model results from (a) is also included in (b).
To evaluate the weak obstacle model in the earlier stages of aging, the evolution of $r$ during aging at 180°C was estimated by fitting a square relationship (i.e. $r = \sqrt{r_o^2 + kt}$ where $r_o = 1 \times 10^{-9}$ m and $k = 7 \times 10^{-23}$ s$^{-1}$) to the TEM data for $r$. The results were used to obtain the model predictions for the initial stages of aging at 180°C. As shown in Figure 6.11(b), the model predictions agrees very well with the experimental data.

### 6.2.5.4 Comparison of Strong and Weak Obstacle Models

The above findings are readily explainable by considering the breaking angles estimated in section 6.2.4.1. For the early stages of aging, where the breaking angles are 120° or larger, the evolution of the yield strength may be very well described by the weak obstacle model. However, the accuracy of model predictions decreases as the angle become smaller by further aging. The strong obstacle model, on the other hand, very well describes the evolution of the yield strength for the entire aging process in the temperature range of 160-220°C, as the breaking angles are estimated to be approximately 120° for the early stages and decrease continuously during aging.

Better agreement of the strong obstacle model with the experimental data during the advanced stages of aging in the temperature range of 160-220°C is consistent with the direct experimental evidences provided by the TEM *in-situ* straining work in AA6056-T6 [Vivas et al. 1996, 1997a, 1997b & 1998]. Although no average value for the measured breaking angles is reported from that study, the published explicit examples and the figures of the strained microstructure provide features of moderately strong obstacles (i.e. breaking angles of smaller than 120°, but well above 0°). The better model predictions with the weak obstacle assumption during the initial stages of aging, is consistent with the fact that the precipitates are initially small. Moreover, the microstructures during the early stages of aging consist of large
proportions of spherical GP zones (see section 5.2.1.3), which may be very well regarded as weak obstacles. As the aging process proceeds, the precipitates become larger and the relative proportions of β", compared to spherical GP zones, i.e. \( \frac{f_\beta}{f_{\text{SGPZ}}} \), increase. This process can be considered as a gradual transition from weak to strong obstacles. A transition from \( f^{1/2}r^{1/2} \) dependence for the critical resolved shear stress to \( f^{1/2} \) proportionality, by the change in the particle size, has also been reported in Al-Zn alloys containing coherent precipitates [Haberkorn and Gerold 1966, Gerold 1979]. Gerold [1979] has attributed this behaviour in Al-Zn alloys to two possible mechanisms: (a) the changes in the shape of the particles from spheres to oblate ellipsoids, which causes drastic changes in the coherency strain fields, and (b) the changes in the interaction mode of dislocations with the particles due to the changes in the nature of the particles. It is speculated that the weak obstacle model may better describe the aging processes at low temperatures where the relative volume fractions of spherical GP zones may be significant for the initial as well as more advanced stages of aging.

In summary, although the ideal model would include transition from weak to strong obstacles, experimental determination of the size evolution and the transition radius would not be justifiable for the process modeling purposes. This is especially impractical considering that the spherical GP zones are not resolvable by conventional TEM (characterization of the microstructural evolution through SAXS has also been found not suitable for this alloy system [Deschamps 1998]). Having shown that the strong obstacle model gives good predictions for the initial stages of aging, as well as excellent predictions for the more advanced stages of aging, it is considered a suitable model for predicting yield strength of AA6111 for the entire aging process in the temperature range of 160-220°C. Therefore, only the strong obstacle model is examined in the following section for the yield strength predictions during the artificial aging of the naturally aged material.
6.3 Modeling of Yield Strength – Naturally Aged Material

The aim is to model the aging processes for the materials with variable levels of natural aging. Modeling follows the same basic principles as that for the solution treated material. The relationships for the evolution of the microstructural variables, however, should be determined according to the behaviour of the naturally aged material.

6.3.1 Precipitation Strengthening

The material response equation, as well as the relationships for the obstacle strength and spacing (strong obstacle model) are the same as those for the solution treated material. Explicitly they are:

Response equation: \[ \sigma_{ppt} = \frac{MF}{bL} \] (6.9)

\[ F \text{ for } r < r_{\text{peak}} : \]
\[ F = \frac{r}{r_{\text{peak}}} F_{\text{peak}} \] (6.11)

\[ F \text{ for } r_{\text{peak}} \leq r \leq r_{c} : \]
\[ F = \left( \frac{r}{r_{\text{peak}}} \right)^m F_{\text{peak}} \] (6.12)

\[ F \text{ for } r \geq r_{c} : \]
\[ F = 2\Gamma \] (6.13)

\[ L \text{ for strong obstacles:} \]
\[ L = \left( \frac{2\pi}{f} \right)^{1/2} r \] (6.23)

6.3.1.1 Estimation of Volume Fraction

The microstructure of the naturally aged material at the start of artificial aging consists of clusters/zones that have formed during natural aging. These clusters tend to dissolve during artificial aging, with a rate dependent on the aging temperature. The concept of the concurrent dissolution and precipitation processes during artificial aging of naturally aged material has been
introduced in section 5.2.2.3. A schematic presentation of the heat effects due to the simultaneous dissolution and precipitation processes, which according to this concept, give rise to the isothermal calorimetry trace of the naturally aged material, has also been shown in Figure 5.33. The proposed deconvolution of the isothermal trace to the dissolution and precipitation events can lead to modeling of the volume fraction evolution for the two concurrent processes. The following method is proposed for this purpose.

**Deconvolution of Isothermal Calorimetry Traces**

Isothermal calorimetry traces for the T4 material, aged at 180°C, 200°C and 220°C, have been used for the analysis. The T4 material used for these calorimetry experiments has been naturally aged for more than two years. Therefore, as a good approximation, it is assumed that the natural aging process is complete at the beginning of artificial aging and the relative volume fraction of the natural aging zones, \( f_r^0 \), is 1.

**Precipitation**

As for the solution treated material, the precipitation process during artificial aging is considered to follow the JMAK kinetics:

\[
 f_{rm} = 1 - \exp(-kt^n) \quad \text{(6.56)}
\]

where \( f_{rm} \) is the relative volume fraction of the precipitates. Differentiation of equation (6.56) gives:

\[
 \frac{df_{rm}}{dt} = knt^{n-1} \exp(-kt^n) \quad \text{(6.57)}
\]

\( f_{rm} \), on the other hand, is related to the fraction of the positive heat effect, due to the precipitation process, during isothermal calorimetry:
As in the case of the solution treated material, \( t_{\text{peak}} \) is the time to reach the zero heat evolution, which corresponds to the peak-age condition. Differentiating and re-arranging equation (6.58) gives:

\[
\frac{dQ_{\text{ppt}}}{dt} = A_{\text{ppt}} \frac{df_{\text{p}}}{dt} \tag{6.59}
\]

Replacing equation (6.57) in (6.59):

\[
\frac{dQ_{\text{ppt}}}{dt} = A_{\text{ppt}}knt^* \exp(-kt^*) \tag{6.60}
\]

Equation (6.60), therefore, governs the precipitation counterpart of the isothermal trace.

**Dissolution**

The kinetics of dissolution of the natural aging zones is described according to the mathematical models developed for the diffusion-controlled dissolution of a second phase particle in an infinite matrix [Aaron 1968, Whelan 1969, Aaron and Kotler 1971]. The time dependence of the particle size for a planar precipitate, considering one-dimensional diffusion, is given by [Whelan 1969]:

\[
\frac{dr}{dt} = -\frac{\eta}{2} \left( \frac{D}{\pi t} \right)^{1/2} \tag{6.61}
\]

where \( r \) is the half-thickness of the precipitate and \( D \) is the diffusion coefficient. \( \eta \) is related to the solute concentrations in the matrix, \( C_M \), and at the matrix-precipitate interface, \( C_i \), as well as the precipitate composition, \( C_P \):
\[ \eta = 2 \left( \frac{C_f - C_M}{C_p - C_f} \right) \]  \hspace{1cm} (6.62)

The kinetics of dissolution of a spherical precipitate, on the other hand, is given by [Whelan 1969, Aaron and Kotler 1971]:

\[ \frac{dr}{dt} = -\frac{\eta D}{2r} - \frac{\eta D}{2} \left( \frac{D}{\pi t} \right)^{1/2} \]  \hspace{1cm} (6.63)

where \( r \) is the radius at time \( t \) of the dissolving precipitate. It is seen that the dissolution rates of the spherical precipitate and the planar precipitate are different in the term \( \frac{\eta D}{2r} \). Whelan [1969] indicates that \( \frac{\eta D}{2r} \) term arises from the steady-state part of the diffusion field, whereas, \( \frac{\eta}{2} \left( \frac{D}{\pi t} \right)^{1/2} \) term stems from the transient part of the diffusion field, emphasizing that the steady-state diffusion does not contribute to the dissolution rate in the one-dimensional case.

Considering that in the present alloy, the natural aging zones are clusters of only a few solute atoms [Murayama & Hono 1999], it is most likely that a steady-state condition [Shewmon 1969] is not established during their dissolution process. Therefore, the dissolution process of the natural aging zones can be closely approximated by assuming \( \frac{\eta D}{2r} = 0 \) in equation (6.63). Having chosen the dissolution model, the time dependence of \( r \) can be obtained by integration of equation (6.61) [Whelan 1969]:

\[ r = r_0 - \frac{\eta}{\pi^{1/2}}(Dt)^{1/2} \]  \hspace{1cm} (6.64)

where \( r_0 \) is the initial radius of the precipitate. Following Nolfi et al. [1969] and the cell concept (see section 2.5), the initial volume fraction of the dissolving zones, i.e. \( f_i \), can be defined as:

\[ f_i = \frac{r_i^3}{r_s^3} \]  \hspace{1cm} (6.65)
where $r_s$ is the radius of the cell containing a single zone (see Figure 2.4). Similarly the volume fraction of the natural aging zones at time $t$ during artificial aging, $f_{NAZ}$, can be defined as:

$$f_{NAZ} = \frac{r^3}{r_s^3}$$ \hfill (6.66)

The relative volume fraction of the natural aging zones during artificial aging, $f_{rNAZ}$, can then be expressed by:

$$f_{rNAZ} = \frac{f_{NAZ}}{f_i} = \frac{r^3}{r_o^3}$$ \hfill (6.67)

Replacing equation (6.64) in (6.67), the relative volume fraction of the natural aging zones during artificial aging is obtained as:

$$f_{rNAZ} = (1 - \frac{\eta D^{1/2}}{\pi^{1/2} r_o^{3/2}} t^{1/2})^3$$ \hfill (6.68)

For simplicity, the temperature dependent factor $B$ is defined as:

$$B = \frac{\eta D^{1/2}}{\pi^{1/2} r_o^{3/2}}$$ \hfill (6.69)

Hence equation (6.68) can be re-written as:

$$f_{rNAZ} = (1 - B t^{1/2})^3$$ \hfill (6.70)

Differentiating equation (6.70):

$$\frac{df_{rNAZ}}{dt} = -\frac{3B}{2} t^{-1/2} (1 - B t^{1/2})^2$$ \hfill (6.71)

Alternatively, the fraction of the natural aging zones that is dissolved during artificial aging, i.e. $(1 - f_{rNAZ})$, can be related to the dissolution counterpart of the isothermal calorimetry trace for the T4 material, i.e. $\frac{dQ_{NAZ}}{dt}$: 

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where \( t_{\text{dis}} \) is the time when the dissolution process finishes. It should be noted that the heat evolution for dissolution, and hence the area under the curve, is a negative value. Then, as expected, \((1 - f_{\text{Naz}})\), being the ratio of two negative values, is positive. Equation (6.72) can also be written in the differential form:

\[
\frac{dQ_{\text{Naz}}}{dt} = -A_{\text{dis}} \frac{df_{\text{Naz}}}{dt}
\]  

(6.73)

Now, replacing equation (6.71) in equation (6.73) gives the relationship for the kinetics of dissolution:

\[
\frac{dQ_{\text{Naz}}}{dt} = \frac{3BA_{\text{dis}} t^{-1/2}}{2} \left(1 - Bt^{1/2}\right)^2
\]

(6.74)

Having known that as the dissolution process approaches completion, \( \frac{dQ_{\text{Naz}}}{dt} \) approaches zero, the time for complete dissolution, \( t_{\text{dis}} \), can be found:

\[
\frac{dQ_{\text{Naz}}}{dt} = 0 \Rightarrow 1 - Bt_{\text{dis}}^{1/2} = 0 \Rightarrow t_{\text{dis}} = \frac{1}{B^2}
\]

(6.75)

Concurrent Dissolution and Precipitation

The total heat evolved can be modeled by combining equations (6.60) and (6.74):

\[
\frac{dQ}{dt} = \frac{dQ_{\text{ppt}}}{dt} + \frac{dQ_{\text{Naz}}}{dt}
\]

(6.76)

Therefore,

\[
\frac{dQ}{dt} = A_{\text{ppt}}knt^{n-1} \exp(-kt^n) + \frac{3BA_{\text{dis}} t^{-1/2}}{2} \left(1 - Bt^{1/2}\right)^2
\]

(6.77)
The unknown parameters $A_{ppt}$ and $A_{dis}$ can be obtained directly from the experimental isothermal calorimetry traces for the solution treated and T4 material:

$$A_{ppt} = \text{the area under the trace for solution treated material}$$

$$A_{T4} = \text{the area under the trace for T4 material}$$

$$A_{dis} = A_{T4} - A_{ppt}$$

Furthermore, from the results obtained for the solution treated material, we can assign the JMAK time exponent:

$$n = 1$$

This is also consistent with the experimental observation of the growth of needle-shape β” and lath-shape Q’ [Christian 1975, Doherty 1996] during artificial aging of the naturally aged material (Table 5.2). By pre-determination of $n$, the number of parameters to be obtained by curve fitting reduces to two, i.e. $k$ and $B$. It should be noted that in the curve fitting procedure, the second term in equation (6.77) should be equated to zero for $t > t_{dis}$.

The typical values obtained for $A_{ppt}$, $A_{dis}$, $k$ and $B$ at different temperatures are listed in Table 6.2. Figure 6.12 shows the curves obtained for the dissolution and precipitation counterparts as well as their summation according to equation (6.77), along with the experimental isothermal calorimetry trace, for the T4 material aged at 180°C. The net curves fitted according to equation (6.77) for other temperatures as well as the corresponding experimental traces are shown in Figure 6.13. It is interesting to see that the shapes of the experimental traces are very well simulated with the fitted curves. It is also observed that the predicted time for the dissolution of the natural aging zones during aging at 180°C is ~ 3-4 hours. This result is consistent with the suggested time for the dissolution of natural aging zones from the analysis of the temperature dependence of the yield strength [Esmaeili et al. 2000].
Table 6.2 – Parameters involved in determination of the relative volume fraction of precipitates and natural aging clusters/zones during artificial aging.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$B$ (s$^{-1/2}$)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$A_{ppt}$ (J/g)</th>
<th>$A_{dis}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.0064</td>
<td>0.00011</td>
<td>11.4</td>
<td>3.6</td>
</tr>
<tr>
<td>200</td>
<td>0.0304</td>
<td>0.00034</td>
<td>9.7</td>
<td>2.5</td>
</tr>
<tr>
<td>220</td>
<td>0.0423</td>
<td>0.00085</td>
<td>10.4</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Figure 6.12 – The isothermal calorimetry trace for AA6111-T4 at 180°C and the curve fitted according to equation (6.77). The dissolution and precipitation counterparts of the fitted curve are also shown.
Figure 6.13 – The isothermal calorimetry traces for AA6111-T4 and the fitted curves according to equation (6.77) at (a) 200°C and (b) 220°C.
Interestingly, the estimated kinetics of precipitation and the time for the dissolution of the natural aging zones are also in close agreements with the results obtained from the analysis of the evolution of electrical resistivity. The estimated relative volume fraction of the precipitates formed during aging for 1 hour at 180°C is also consistent with the quantitative TEM analysis. These results will be discussed later in this section.

**Temperature Dependence of k and B**

As in the case of the solution treated material, an Arrhenius-type relationship can be formulated for $k$:

$$k = k_0 \exp(-Q_{ppl} / RT)$$  \hspace{1cm} (6.78)

where $k_0$ is the pre-exponential constant and $Q_{ppl}$ is the apparent activation energy related to the precipitation process.

In the case of dissolution, considering equation (6.69), the temperature dependence of $B$ can be modeled according to the temperature dependence of $\eta D^{1/2}$. Being the diffusion coefficient, $D$, has an Arrhenius-type relationship with temperature:

$$D = D_0 \exp(-Q_d / RT)$$  \hspace{1cm} (6.79)

where, $D_0$ is the proportionality constant factor and $Q_d$ is the activation energy for diffusion of the solutes in the matrix. Also, using the assumptions involved in formulating equations (6.61) and some practical approximations, a simple relationship between $\eta$ and $T$, and consequently between $B$ and $T$ can be obtained. First, since the dissolution model is based on the assumption that the precipitate-matrix interface is always at equilibrium [Whalen 1969, Aaron 1968], $C_f$ can be regarded as the metastable solvus boundary for the zones. Second, the precipitate composition, i.e. $C_p$, is assumed to remain constant during dissolution [Aaron and Kotler 1971] and $C_p >> C_f$ [Whelan 1969]. Furthermore, since in the naturally aged condition, the matrix, of
already a dilute alloy, is depleted from the solutes, the assumption of \( C_I \gg C_M \) can be a good approximation. Hence, equation (6.62) can be simplified as:

\[
\eta \equiv \frac{2C_I}{C_p}
\]  
(6.80)

\( C_I \), as the only variable in equation (6.80), can be related to temperature [Swalin 1962]:

\[
C_I = c \exp\left(-\frac{Q_s}{RT}\right)
\]  
(6.81)

where \( c \) is the proportionality constant and \( Q_s \) is the enthalpy of solution of the natural aging zones (i.e. solvus boundary enthalpy). Using equations (6.69), (6.79), (6.80) and (6.81), the temperature dependence of \( B \) can be obtained as:

\[
B \propto \exp\left(-\frac{Q_s}{RT}\right)\left[\exp\left(-\frac{Q_d}{RT}\right)\right]^{1/2}
\]  
(6.82)

In other words, \( B \) can be modeled as:

\[
B = B_0 \exp\left(-\frac{Q_{dis}}{RT}\right)
\]  
(6.83)

where,

\[
Q_{dis} = Q_s + \frac{Q_d}{2}
\]  
(6.84)

and \( B_0 \) is the pre-exponential constant.

Using the data obtained for \( k \) and \( B \) at 180°C, 200°C, and 220°C, and plotting their Arrhenius-type relationships with temperature, the kinetic parameters for the precipitation and dissolution processes are determined, Figure 6.14. It should be noted that by repeating the curve fitting procedure (i.e. applying equation 6.77), a series of values, though very close, are obtained for \( k \) and \( B \). The scatter in the data for \( B \) and \( k \) results in a range of activation energies (~±10 kJ/mole), with the average values of: \( Q_{dis} = 88 \) kJ/mole and \( Q_{ppt} = 95 \) kJ/mole. Considering that the activation energies for diffusion of Mg and Si in aluminum are approximately 130 kJ/mole [Hatch 1984], \( Q_s \), according to equation (6.84), should fall in the
Figure 6.14 – Arrhenius plots for $B$ and $k$. 
approximate range of 10-30 kJ/mole. Having, determined $k$ and $B$, the relative volume fraction of precipitates and natural aging zones, i.e. $f_{\text{pp}}$ and $f_{\text{T4AZ}}$, are obtained according to equations (6.56) and (6.70). The typical evolutions of $f_{\text{pp}}$ and $f_{\text{T4AZ}}$ during artificial aging of the T4 material are shown in Figure 6.15. The evolution of the relative volume fraction of precipitates, during artificial aging, for the T4 and solution treated materials are compared in Figure 6.16. It is clearly shown that the precipitation process for the T4 material is significantly slower than that of the solution treated material. This is consistent with the experimental results discussed in Chapter 5. The possible reasons for this behaviour has also been discussed in section 5.2.2.1.

Estimation of the Volume Fraction of Natural Aging Zones – Variable Levels of Natural Aging

The volume fraction of the natural aging zones at the beginning of artificial aging, $f_{\text{T4NA}}$, is dependent on the time over which the material has been naturally aged, i.e. $t_{\text{NA}}$. Assuming that after two years of natural aging the cluster/zone formation is complete, the relative volume fraction of these clusters/zones at the beginning of the artificial aging process, $f_{r}^{0}$, can be defined as:

$$f_{r}^{0} = \frac{f_{\text{T4NA}}}{f_{2y}}$$  \hspace{1cm} (6.85)

where $f_{2y}$ is the volume fraction of the natural aging zones formed during natural aging for two years. Therefore, when $t_{\text{NA}} < 2$ years, the material is partially naturally aged, i.e. $f_{r}^{0} < 1$. For a partially naturally aged material, as a consequence, the volume fraction of the natural aging zones during artificial aging, is less than that of the T4 material at the same time of artificial aging.
Figure 6.15 – Evolution of the relative volume fraction for precipitation of hardening phases (i.e. ppt) and dissolution of natural aging zones (i.e. NAZ) during aging at (a) 180°C and (b) 200°C of the T4 material.
Figure 6.16 – Evolution of the relative volume fraction of precipitates during artificial aging at 180°C of the T4 and solution treated materials.
In order to model the kinetics of cluster dissolution for the partially naturally aged materials, it is assumed that the size of the natural aging zones at the beginning of artificial aging, i.e. \( r_0 \), is constant and independent of the duration of the natural aging time. This assumption, as discussed in section 5.2.1.2, is supported by reasonable experimental evidence. It is also assumed that the value of \( \eta \) (equation 6.62) for the clusters/zones formed during variable times of natural aging is similar. Therefore, the dissolution rate constant, i.e. \( B \), according to equation (6.69) is the same for the natural aging zones, regardless of the duration of the natural aging process. Hence, the kinetics of dissolution of the zones during the artificial aging is similar for all naturally aged materials. In other words, the dissolution kinetics is given by equation (6.70) for all naturally aged materials. Hence, the only difference in the volume fraction of the zones, for materials with various levels of natural aging, during artificial aging comes from the initial volume fraction of the zones, i.e. \( f_r^0 \). The effect of a high or low \( f_r^0 \) is reflected and unchanged through the entire artificial aging process until the zones are completely dissolved. This concept can be formulated as:

\[
h_{\text{NAZ}} = f_r^0 f_{\text{NAZ}}
\]  

(6.86)

where \( h_{\text{NAZ}} \) is the relative volume fraction of the natural aging zones during artificial aging of the naturally aged material (any natural aging time), and \( f_{\text{NAZ}} \), as before, is the relative volume fraction of the natural aging zones during artificial aging of a two-year naturally aged material (i.e. T4 material in this study). It is obvious that \( f_r^0 = 1 \) for \( t_{\text{NA}} \geq 2 \) years. \( f_r^0 \), as a function of natural aging time, is determined through calibration procedure described in section 6.3.4.1.

Evolution of the volume fraction of the precipitates during artificial aging for a partially naturally aged material is also assumed to be the same as that of the T4 material. This assumption has been discussed in section 5.2.2.1 based on the similarities for the dissolution reactions.
It is interesting now to compare the relationship obtained for the kinetics of precipitation from the isothermal calorimetry method with the kinetics information obtained from the resistivity analysis.

The relative volume fraction of precipitates during artificial aging has been obtained by applying the JMAK model to the isothermal calorimetry results. Accordingly, the following relationship has been obtained for aging at 180°C:

\[
f_{\text{prec}} = 1 - \exp(-1.1 \times 10^{-4} t)
\]  

(6.87)

where \( t \) is in seconds (see Table 6.2). The proposed model for the deconvolution of the calorimetry data has also suggested that the time for the complete dissolution of the natural aging zones at 180°C is \( \sim 3-4 \) hours. Hence, the analysis of the resistivity data (as discussed in Chapter 5) should provide information on the kinetics of solute depletion beyond 4 hours of aging (assuming that the precipitates are large and do not contribute to the electron scattering after 4 hours of aging). Now referring to the analysis described in section 5.2.1.2, equation (5.16) is applied to the resistivity data for the 2-week naturally aged sample for 4 to 10 hours of aging (10 hours is the peak-age condition). The following relationship is obtained:

\[
\rho_r = 15.98 + 6.79 \exp(-1.1 \times 10^{-4} t)
\]  

(6.88)

where the units of resistivity and time are n\( \Omega \)m and s, respectively. According to Matthiessen's law the resistivity change is proportional to the solute depletion, thus \( k = 1.1 \times 10^{-4} \) s\(^{-1} \) can also be used as the rate for solute depletion during this aging condition. Hence, the above rate can be used in equation (5.12) (which is essentially the JMAK model with a pre-assumption of \( n = 1 \)) to obtain the fraction of solute depletion or equivalently the relative volume fraction of precipitates [Shercliff and Ashby 1990]:
\[ f_r = \frac{C_i - C_t}{C_i - C_e} = 1 - \exp(-kt) = 1 - \exp(-1.1 \times 10^{-4} t) \] (6.89)

Interestingly, the rate constants in equations (6.87) and (6.89) are very similar, and thus, the evolution of \( f_r \) obtained from the isothermal calorimetry is in excellent agreement with the analysis of the electrical resistivity in the range of 4-10 hours of aging at 180°C.

Now when equation 5.17 is applied to the resistivity data in the range of 0-4 hours the resulting rate constant is smaller than the rate constant obtained from the isothermal calorimetry for the entire underaging period (i.e. \( k = 1.1 \times 10^{-4} \text{ s}^{-1} \)):

\[ \rho_r = 15.25 + 5.7 \exp(-6.7 \times 10^{-5} t) \] (6.90)

where the units of resistivity and time, as before, are n\(\Omega\)m and s, respectively. This indicates that small zones are still present and contribute to the electron scattering during the first few hours of aging at 180°C. The presence of the natural aging zones as well as their continuous dissolution during the first few hours of aging can both contribute to the slower kinetics of the resistivity decay (when compared with the aging period of 4-10 hours). The above comparison illustrates that the predictions for the kinetics of dissolution and precipitation obtained by the proposed calorimetry model is in agreement with the analysis of the electrical resistivity data.

Comparison of the relative volume fraction of precipitates obtained by the quantitative TEM analysis and isothermal calorimetry, on samples aged at 180°C after 2 weeks of natural aging, also illustrates the excellent agreement between the prediction of the isothermal calorimetry model and the independent experimental results, Table 6.3. As discussed earlier, the predicted time for the dissolution of the natural aging zones at 180°C is also consistent with the results obtained from the analysis of the temperature dependence of the yield stress [Esmaeili et al. 2000]. Hence, the agreement between the results obtained by the proposed isothermal calorimetry model and the other independent techniques validates the modeling of the kinetics of
Table 6.3 – The values obtained for $f_r$ from the isothermal calorimetry and TEM analysis. The samples have been aged at 180°C after 2 weeks of natural aging.

<table>
<thead>
<tr>
<th>Time at 180°C (hr)</th>
<th>Isothermal Calorimetry</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
precipitation, as well as the kinetics of dissolution of the natural aging clusters, during artificial aging of the naturally aged materials.

6.3.1.2 Estimation of $\sigma_{ppt}$ for Underage and Peak-age Conditions

**Strengthening due to the Natural Aging Zones**

Due to the fact that the natural aging zones are clusters of a few solute atoms, with no defined structure, they can be considered as weak obstacles. Therefore, their contribution to the yield strength, $\sigma_{NAZ}$, can be assumed to obey Friedel statistics:

$$\sigma_{NAZ} \propto r_{NAZ}^{1/2} f_{NAZ}^{1/2}$$

(6.91)

where $r_{NAZ}$ is the average radius of the zones. Since these zones are very small, the change in $r$ is very small compared to the change in $f$ (e.g. $r_{NAZ}$ may vary from 1 nm to 0.2 nm, at the same time $f_{NAZ}$ changes from 0.99 to 0.01). Hence, $r_{NAZ}$ in equation (6.91) can be considered constant. Therefore, equation (6.91) reduces to:

$$\sigma_{NAZ} \propto f_{NAZ}^{1/2}$$

(6.92)

To evaluate $\sigma_{NAZ}$ for materials with variable levels of natural aging, a general form of relationship (6.92) can be used:

$$\sigma_{NAZ} = C_6 (h_{r_{NAZ}})^{1/2}$$

(6.93)

Therefore using equation (6.86), equation (6.93) can be written in the expanded form:

$$\sigma_{NAZ} = C_6 (f_{r}^{0} f_{r_{NAZ}})^{1/2}$$

(6.94)

**Strengthening Due to the Precipitates Formed during Artificial Aging**

As discussed in section 6.2.5.4, only strong obstacle case is considered. Hence, equation (6.34) is used to evaluate $\sigma_{ppt}$.
Since the peak-aged naturally aged material has a coarser microstructure (i.e. larger $r_{\text{peak}}$) than the peak-aged solution treated material (section 5.2.3.3), $C_7$ is slightly different from $C_1$.

### 6.3.1.3 Estimation of $\sigma_{\mathrm{ppt}}$ for Overaging Condition

$\sigma_{\mathrm{ppt}}$ for the overaging condition can be estimated using equation (6.38) or (6.40), depending on the extent of overaging:

- $r_{\text{peak}} \leq r \leq r_{c}$:
  \[
  \sigma_{\mathrm{ppt}} = \frac{Mf_{\text{peak}} f_{r_{\text{peak}}}}{b(2\pi)^{1/2} r_{\text{peak}}} = C_8 r^{-1} 
  \]  
  (6.96)

- $r \geq r_{c}$
  \[
  \sigma_{\mathrm{ppt}} = \frac{Mf_{\text{peak}} f_{r_{\text{peak}}}}{b(\pi/2)^{1/2} r_{\text{peak}}} = C_9 r^{-1} 
  \]  
  (6.97)

Again due to the difference in $r_{\text{peak}}$, $C_8$ is slightly different from $C_3$. On the other hand, $C_9$, being independent of size, is equal to $C_5$.

### 6.3.2 Solid Solution Strengthening

Equation (6.51), which was derived to estimate the solid solution strengthening for the solution treated material, should be modified to take into account of the solute depletion for both natural aging zones and precipitates:

\[
\sigma_{\mathrm{ss}} = \sigma_{\mathrm{0ss}} [1 - (h_{r_{\text{peak}}} + f_{r_{\text{ppt}}})]^{2/3} 
\]  
(6.98)

Using equation (6.86), equation (6.98) can be re-written in the expanded form:
6.3.3 Overall Strength

The linear addition rule, for considering the contributions from the precipitates, the solid solution and the pure matrix, is also applied for the artificial aging of the naturally aged material:

\[
\sigma_{ss} = \sigma_{0ss} \left[ 1 - (f_r^0 f_{r0,z} + f_{r,w}) \right]^{2/3}
\]

(6.99)

where \( \sigma_{r0} \) is the contribution from the mixture of precipitates and natural aging zones or the precipitates alone, depending on whether the two kinds of obstacles coexist or the natural aging zones have completely dissolved. Hence, an appropriate superposition law is needed to estimate \( \sigma_{ppt} \), when the two types of obstacles are present in the microstructure. Considering the evolution of the microstructure during artificial aging, which consists of a variable mixture of moderately strong (i.e. precipitates) and weak (i.e. natural aging zones) obstacles, the so-called Pythagorean superposition is considered the most appropriate addition rule [Brown and Ham 1971, Ardell 1985]:

\[
\sigma_{ppt} = (\sigma_{ppt}^2 + \sigma_{N4Z}^2)^{1/2}
\]

(6.101)

6.3.4 Calibration of the Model

6.3.4.1 Underage and Peak-age Condition

The constant parameters that are needed to estimate \( \sigma_y \) during artificial aging are: \( C_6 \), \( C_7 \) and \( f_r^0 \). \( C_6 \) is evaluated using the experimental results for the T4 material (2-year naturally aged), i.e. at the start of artificial aging:

\[
\sigma_y = 170 \text{ MPa}
\]
It is assumed that after 2 years of natural aging:

\[ \sigma_{ss} = 0 \]

It is also known that:

\[ \sigma_i = 10 \text{ MPa} \]

Therefore,

\[ \sigma_{NAZ} = 160 \text{ MPa} \]

Having assumed that at the start of the artificial aging process of the T4 material,

\[ f_r^0 = 1 \text{ and } f_{NAZ} = 1, \]

\( C_6 \) can be estimated according to equation (6.94):

\[ C_6 = \sigma_{NAZ} = 160 \text{ MPa} \]

It was previously shown that the peak strength for the solution treated material is almost constant in the temperature range of 160°C-220°C. Assuming a similar behaviour for the naturally aged material, the peak strength is expected to be constant in the range of 160°C-220°C. The tensile test results show that the peak yield strength for the T4 material aged at 180°C is 325 MPa. Therefore, at the peak age condition (i.e. \( f_{r_{pp}} = 1 \) and \( \sigma_{ss} = 0 \)):

\[ \sigma_{pp} = 315 \text{ MPa} \]

Hence, using equation (6.95):

\[ C_7 = \frac{\sigma_{pp}}{f_r^{1/2}} = 315 \text{ MPa} \]

_Evolution of the Relative Volume Fraction of Zones during Natural Aging_

An analytical method is introduced to estimate \( f_r^0 \) through the experimental data for the evolution of yield strength during natural aging. As it was shown in section 5.1.1.1, the
evolution of yield strength during natural aging can be modeled by a logarithmic relationship with time:

\[ \sigma_y = a \ln t_{NA} + b \]  

(6.102)
The constants according to the logarithmic fit to the yield strength data are: \( a = 12.3 \) MPa for \( t_{NA} \) in hours, and \( b = 67 \) MPa. On the other hand, \( \sigma_y \) has contributions from the clusters/zones, i.e. \( \sigma_{NAZ} \), the solid solution, i.e. \( \sigma_{ss} \), as well as the intrinsic strength of aluminum:

\[ \sigma_y = \sigma_i + \sigma_{ss} + \sigma_{NAZ} \]  

(6.103)
Recalling that natural aging zones are considered weak obstacles, equation (6.91) is applicable for the natural aging process. As discussed before (section 5.2.1.2), the radius of these clusters/zones during natural aging can be considered constant. Hence,

\[ \sigma_{NAZ} = C^0 \left(f_r^0\right)^{1/2} \]  

(6.104)
where \( C^0 \) is the proportionality constant. Using the value of \( \sigma_{NAZ} \) for the two-year naturally aged material (i.e. \( f_r^0 = 1 \)):

\[ C^0 = 160 \text{ MPa} \]
Assuming that the evolution of \( \sigma_{ss} \) during natural aging follows a relationship similar to equation (6.51):

\[ \sigma_{ss} = \sigma_{0ss} \left(1 - f_r^0\right)^{2/3} \]  

(6.105)
Replacing equations (6.104) and (6.105) in equation (6.103) and substituting for the constants \( \sigma_i, C^0 \) and \( \sigma_{0ss} \):

\[ \sigma_y = 10 + 52\left(1 - f_r^0\right)^{2/3} + 160\left(f_r^0\right)^{1/2} \]  

(6.106)
where \( \sigma_y \) is in MPa. Equating equation (6.102) with equation (6.106) will result in a relationship between \( f_r^0 \) and \( t \):
12.3 \ln t_{\text{NA}} + 67 = \sigma_y = 10 + 52(1 - f_r^0)^{2/3} + 160(f_r^0)^{1/2} \tag{6.107}

Equation (6.107) can be solved for any time $t_{\text{NA}}$ using an iteration method (e.g. Newton’s Method), to obtain $f_r^0$ vs. $t_{\text{NA}}$. Finally, as shown in Figure 6.17, plotting $\ln \ln \left( \frac{1}{1 - f_r^0} \right)$ vs. $\ln t_{\text{NA}}$ gives a straight line, resulting in a JMAK relationship for $f_r^0$:

$$f_r^0 = 1 - \exp(-0.02t_{\text{NA}}^{0.5}) \tag{6.108}$$

where $t_{\text{NA}}$ is in hours.

### 6.3.4.2 Overage Condition

As it was shown in section 5.2.2.2, the kinetics of overaging for the naturally aged and solution treated samples during artificial aging are very similar. Hence, it is reasonable to assume that the evolution of $r$ during overaging for the naturally aged material obeys the same kinetics as that for the solution treated material (section 6.2.4.2). Therefore,

$m = 0.6$

Also, from the TEM data (using the cross sectional area of $\beta^\prime\prime$ for 7 hours of aging, Table 5.2):

$r_{\text{peak}} \equiv 1.9 \text{ nm}$

Hence, using equation (6.96) for the peak-age condition:

$$C_8 = \sigma_{\text{ppt}} r^{1-m} = 102285 \text{ Nm}^{-1.6}$$

$$C_9 = C_5 = 0.8 \text{ Nm}^{-1}$$
Figure 6.17 – The plot of $\ln \ln \left( \frac{1}{1 - f_r^\theta} \right)$ vs. $\ln t_{NA}$. 
6.3.5 Model Implementation

The modeling and experimental results are compared in Figure 6.18(a) for the T4 material aged at 180°C. Excellent agreement is shown between the modeling results and the experimental data. Figure 6.18(b) shows the model predictions for the contributions from the natural aging zones and the precipitates to the overall yield strength of the T4 material during aging at 180°C. As expected, the contribution from the natural aging zones to the overall yield strength is significant during the earlier stages of aging. However, it declines as the aging process proceeds and the zones approach complete dissolution (i.e. ~ 4 hours).

6.3.5.1 Validation of the Model

The model is validated by comparing its predictions with a series of independent experimental results, for a combination of natural aging times and artificial aging temperatures. In Figure 6.19, the model predictions are compared with the experimental results, which have been provided by Alcan International, for the artificial aging of T4 material at 140°C, 160°C and 200°C. The agreement between the model predictions and the experimental data is very good in the entire aging period. The model validity is also evaluated for artificial aging of the materials with various levels of natural aging, Figure 6.20. As in the previous cases, the model shows good prediction capabilities. It predicts the effect of different levels of natural aging on slowing down the hardening process. It also proves that the assumption made in the model development for the similarity of the precipitation kinetics, regardless of the level of natural aging, is reasonable for the natural aging times as low as 24 hours. This can be better realized by comparing the model predictions as well as the experimental results for artificial aging at 180°C of materials naturally aged for 24 hours, 2 weeks and 2 years, Figure 6.20(c). The model formulation for the dissolution of natural aging zones, and the attributed role of these zones on
Figure 6.18 – (a) Modeling results and the experimental data for aging at 180°C of the T4 material. (b) Model predictions for the contributions from the natural aging zones (NAZ) and the precipitates (ppt) to the overall yield strength.
Figure 6.19 – Artificial aging of 6111-T4 at 140°C, 160°C and 200°C.

Experimental results courtesy of Alcan International.
Figure 6.20 – Comparison of the model predictions and experimental results for a combination of natural aging times and artificial aging temperatures. (a) Natural aging for 24 hours followed by aging at 180°C, (b) Natural aging for 2 weeks followed by aging at 180°C, (c) Effect of various levels of natural aging on age hardening process at 180°C, (d) Natural aging for 3 days followed by aging at 220°C.
altering the nucleation process during artificial aging (section 5.2.2.1), provide, therefore, a credible explanation to the delayed age hardening process of the naturally aged materials.

6.4 Range of Applicability and Sensitivity of the Model

As previously discussed, the information on the evolution of volume fraction has been obtained from the isothermal calorimetry tests in the range of 160-220°C for the solution treated material and 180-220°C for the T4 material. Therefore, the model predictions are expected to cover these ranges of temperatures. This has been found to be the case for the solution treated material. In the case of the naturally aged material, the model predictions proved to closely approximate the experimental data in the range of 140-220°C. Implementation of the model for the higher or lower temperatures should be followed by the proper determination of the microstructural variables (i.e. $f_r$ for high temperatures and probably both $f_r$ and $r$ for low temperatures).

The model was able to predict the effect of natural aging times as low as 24 hours on the age hardening process. The model may be applicable to natural aging times as low as a few hours (e.g. ~4 hours corresponding to the transition from fast to slow clustering reactions during natural aging, section 5.1.1.2). However, this needs to be verified. For natural aging times less than 1 hour, the aging response of the material is probably better predicted using the basic model developed for predicting the yield strength of the solution treated material.

The assumption of the complete depletion of solutes from matrix when the relative volume fraction reaches unity does not cause a significant error in the estimation of the yield strength. This is due to the fact that the above assumption affects the calibration of the constant factors for both contributions of solid solution strengthening and precipitation hardening. The net effect of the changes in these factors on the overall strength is negligible in the present
system. This can be verified by assuming a reasonable value for the remaining solute concentration at the peak age condition (e.g. 50% of the original composition) and re-applying the calibration procedure to find a new set of the constant factors to estimate $\sigma_{ppr}$ and $\sigma_{ss}$. Using these new factors, the resulting overall strength becomes only slightly smaller (~ 5 MPa) than the corresponding values with the assumption of all solutes being consumed at the peak age condition. Therefore, this is not considered a major source of error.

The yield strength prediction for the underaging conditions is mainly dependent on the accuracy in the value of the relative volume fraction. Hence, the sensitivity of the model to the possible errors in the estimation of the relative volume fraction should be examined. The possible sources of error in estimating the relative volume fraction are:

1. *The time lag in the isothermal calorimetry data:*

   The calorimeter, which is run at the aging temperature of interest, is disturbed in the first 7-9 minutes after introducing the samples and produces no heat evolution data. Therefore, the data is lost in this first 7-9 minutes. Also, the actual heating rate in the sample to reach the set temperature is not known. In other words, the samples may have been exposed to non-isothermal condition at the very initial stages of aging. However due to the short duration of the initial time lag, compared to the time to reach the zero heat evolution in the temperature range investigated, these effects are not significant. The close agreement between the values of $f_r$ estimated by the isothermal calorimetry method and the DSC method (aging at 180°C) has verified the relative accuracy of the results for the temperatures within the present range of interest. Considering the faster kinetics of precipitation at higher temperatures, a time lag of 7-9 minutes may be an important source of error for the high temperature aging processes (e.g. $T > 220^\circ C$).
2. **Kinetics of precipitation:**

The JMAK model may not be the best choice to describe the precipitation kinetics. Although the JMAK fits to the experimental isothermal calorimetry data, as shown in Figures 6.5 and 6.6, are reasonably good, they do not coincide exactly with the data. Hence, this can be considered as a source of error, although it is small.

3. **Kinetics of dissolution:**

Although the model adapted to describe the dissolution kinetics of the natural aging zones has been based on several simplifying assumptions, it describes the isothermal calorimetry results reasonably well. In addition, the predicted time for the dissolution of zones is in very good agreement with the results obtained through other independent experimental methods. Implementing the proposed kinetics of dissolution in the yield strength model for the naturally aged materials results in very close predictions for the yield strength of materials with variable levels of natural aging.

3. **Curve fitting errors:**

The errors encountered during curve fitting procedures, to obtain the JMAK constant $k$ and the dissolution rate parameter $B$, give rise to errors in determination of the temperature dependence of these parameters, i.e. the values for the apparent activation energies and the corresponding proportionality constants. As a result, a range of values for the activation energies and hence for the corresponding rate constants are obtained. However, since the activation energies are coupled with their own proportionality constants, the overall effects on the evolution of the relative volume fraction, and hence the yield strength model predictions, are not significant.

The sensitivity of the model to the curve fitting errors in determination of $f_c$ is examined in Figure 6.21 for aging at $180^\circ$C. It is found that the sensitivity of the model to the changes in
Figure 6.21 – The model sensitivity to the changes in the estimation of $f_r$. Modeling results are based on the following rate constants: M1: $Q = 58$ kJ/mole, $k_0 = 3280$ s$^{-1}$ (these values have been used for the JMAK fit in Figure 6.5 as well as the modeling results in Figure 6.9), M2: $Q = 55$ kJ/mole, $k_0 = 1195$ s$^{-1}$.
\( f_r \), within the practical limits of error, is small. A series of repeats for the determination of \( f_r \) have shown that the resulting differences in the model predictions are always less than 20 MPa.

6.5 Concluding Remarks

In this chapter, the process model developed for AA6111 as well as the sub-models for describing the microstructural evolution have been introduced, discussed and validated. The main conclusions of the present work and the recommendations for future studies will be summarized in the next chapter.


CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The objective of the present work was to investigate the precipitation hardening behaviour of AA6111 through: (a) obtaining a comprehensive knowledge on the effect of thermal processing on the evolution of microstructure and properties of the alloy, (b) integrating the acquired knowledge with established physical theories and models to develop a new process model to predict the yield strength of the alloy during artificial aging. The thermal processing of interest were (a) artificial aging of the solution heat-treated materials and (b) artificial aging of the materials with variable levels of natural aging. The process model aimed at predicting the evolution of the yield strength of the alloy during the entire aging process. Having met the objective, some important conclusions can be summarized as follows:

- Precipitation Hardening Behaviour

The combination of mechanical and calorimetry studies suggests that the alloy has similar precipitation behaviour in the temperature range of 160-220°C. In addition, the DSC and TEM works identify the main precipitates forming during the underaging process. These precipitates are spherical GP zones, needle-shape β” and lath-shape Q’. The hardening phase is mainly β”, however, spherical GP zones may have important contributions to the yield strength in the very early stages of aging. The overaging reactions probably comprise the transition from β” to Q’ as well as the phase transitions involving Q phase and its precursors. These reactions are accompanied by coarsening of phases. Coarsening of β” starts prior to the peak-age condition.
The precipitation behaviour during artificial aging of the naturally aged material is characterized by a considerably slower kinetics for $\beta''$ precipitation as well as the enhancement of $Q'$ formation and a coarser microstructure, when compared to the case of the material with no prior natural aging. However, the overaging kinetics are found to be very similar for both thermal histories. The slow rate of hardening is attributed to the effect of natural aging clusters/zones on altering the nucleation mechanisms during artificial aging. The resemblance observed for the kinetics of age hardening for materials with variable levels of natural aging can be considered in terms of the similar kinetics of dissolution for natural aging zones regardless of the extent of the natural aging process. It is proposed that this can be explained in terms of the similar sizes of these zones for variable natural aging times. This proposition is supported by the information obtained from the electrical resistivity measurement during natural aging as well as the microscopic observations reported in the literature.

The kinetics of precipitation for the solution treated material is readily determined by using the isothermal calorimetry technique. A new simple analytical procedure is also proposed to obtain the kinetics of precipitation through the DSC results. The results obtained by both methods as well as the results from the quantitative TEM analysis are found to be consistent. The applicability of the electrical resistivity measurement for obtaining information on the kinetics of precipitation is under further investigation. The results are very promising.

**Modeling**

The contribution from precipitation hardening to the overall yield strength is related to the obstacle strength and the effective spacing between the obstacles. A simple evolution law is proposed to describe the change in the obstacle strength during aging, based on the existing theories for the strengthening mechanisms as well as the information obtained for the microstructural evolution and the mechanical behaviour of the alloy. According to the proposed
model the average obstacle strength varies linearly with the average radius of the precipitates up to the peak-age condition, and according to a power law beyond the peak until the obstacles become non-shearable. The linear relationship between the obstacle strength and radius is validated using experimental data. The power-law relationship also gives satisfactory results for the peak-age as well as the aging condition for the shearable to non-shearable transition. Consistent with the characteristics of the dislocation-precipitation interactions in this alloy, the proposed law considers that the shearable to non-shearable transition is not coincident with the peak-age, but it occurs at later stages of overaging. The analysis of the combined modeling-experimental results provides interesting information on the evolution of the obstacle strength and dislocation breaking angles during artificial aging. An analytical procedure is used to obtain the appropriate evolution laws for the effective spacing of strong and weak obstacles, based on the microstructural characteristics of the alloy.

The contribution of precipitation hardening to the yield strength is modeled separately for the cases of strong and weak obstacles. The overall yield strength is obtained by the linear additions of the contributions from precipitation hardening, solid solution strengthening and the intrinsic strength of the matrix. The results obtained for the yield strength evolution according to both strong and weak obstacle models are compared with the experimental values. In agreement with the information obtained for the evolution of the dislocation breaking angles, while the weak obstacle model shows acceptable results for the early stages of aging, the strong obstacle model is found to be applicable for the entire period of aging in the temperature range of 160-220°C. The model is validated by independent experimental results. The applicability of the strong obstacle model for the entire aging period reduces the microstructural variables needed for prediction of the yield strength for the underaging condition to only the relative volume fraction of precipitates. The calibration of the model for the underaging predictions also needs the peak strength value only.
The isothermal calorimetry results are analyzed to obtain the evolution of the relative volume fraction of precipitates during aging, in the temperature range of 160-220°C. The advantages of using isothermal calorimetry method are listed as follows:

(a) The experiment is very simple and inexpensive.
(b) A very small number of tests are required.
(c) The evolution of the relative volume fraction of precipitates reflect the effect of all precipitation reactions, some of which may not be detectable by TEM and other experimental techniques.
(d) The method been shown to describe well the kinetics of precipitation.

A new model is proposed to describe the kinetics of concurrent precipitation and dissolution of natural aging zones during artificial aging of the naturally aged materials. The model is applied to the isothermal calorimetry results of the T4 samples. The slow kinetics of precipitation as well as dissolution of natural aging zones are described by the model. The kinetic information obtained from the model are in very good agreement with the results obtained from the analysis of the electrical resistivity as well the temperature dependence of the yield strength and the quantitative TEM results. The effect of variable levels of natural aging is also considered based on the knowledge obtained on the related microstructural evolution. Prediction of the kinetics of dissolution of the natural aging zones for materials with variable levels of natural aging becomes possible by developing a sub-model to determine the evolution of the relative volume fraction of the clusters/zones during natural aging.

The contributions from natural aging zones, precipitates formed during artificial aging as well as the solid solution strengthening and the intrinsic strength of the matrix are added using the appropriate addition laws. The modeling and experimental results are found to be in very close agreements. The model is validated by excellent agreements with the results of
independent experimental data for different aging temperatures and variable levels of natural aging.

The model will be easily expandable for non-isothermal aging conditions, including multi-step aging treatments in a specified temperature range. It may also be used directly for other Al-Mg-Si-Cu alloys with similar compositions to AA6111 (e.g. AA6056). For other 6000 series alloys, it is suggested that the strong obstacle model can be implemented for yield strength predictions at high temperatures with conducting a small number of isothermal calorimetry tests to characterize the evolution of the relative volume fraction of precipitates. The yield strength predictions for the cases where the hardening precipitates are categorized as weak will need kinetics information for the evolution of both size and the relative volume fraction of precipitates. These ideas as well as other views for future work are summarized in the next section.

7.2 Future Work

The ideas for the future work are divided in two categories of short term and long term prospects.

- Proposals for Short Term Work

- The model is proposed to be implemented for non-isothermal aging conditions involving both solution treated and naturally aged materials. The results can be valuable for industrial processes including ramp and step aging treatments for mechanical property and process optimizations.
- It is proposed that the applicability of the model to other 6000 series alloys as well as some other precipitation hardening systems to be examined.
– The analysis of the electrical resistivity results for obtaining information on the kinetics of precipitation as well as the kinetics of concurrent precipitation and dissolution of clusters are proposed to be completed. This may provide another simple method for obtaining kinetics information as well as further interesting implications for future studies.

☐ Proposal for a Long Term Project

– It is suggested that a precipitation model based on the theories of nucleation, growth and coarsening, as well as the knowledge on the microstructural evolution of AA6111, be developed and coupled with the present process model. This will enable the model to include the effect of particle size distribution and the transition from weak to strong obstacle conditions. It can also provide information on the microstructural evolution for a broad range of temperature. In particular, the joint precipitation-process model can be useful for predicting the effects of low temperature pre-aging processes on the artificial aging response of the material.
REFERENCES


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