CHARACTERIZATION AND MODELING OF DISLOCATION-PRECIPITATION INTERACTIONS IN ALUMINUM ALOYS

By

REZA SHAHBAZIAN YASSAR

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of REZA SHAHBAZIAN YASSAR, and find it satisfactory and recommend that it be accepted.

___________________________________
Chair

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CHARACTERIZATION AND MODELING OF DISLOCATION-PRECIPITATION INTERACTIONS IN ALUMINUM ALOYS

Abstract

by Reza Shahbazian Yassar, Ph.D.
Washington State University
December 2005

Chair: David Field

Current research is aimed towards making contribution in the areas of (i) understanding the details of precipitation-dislocation interactions, (ii) determining the significance of these interactions on the flow stress response, and (iii) on developing a multiscale model which is based on the interaction of dislocations and precipitates. In this research project the precipitation sequence of a precipitation hardened alloy, AA6022, was characterized by means of transmission electron microscopy, differential scanning calorimetry, and hardness measurements. The metastable phases during the isothermal and dynamic decomposition of supersaturated alloy were identified and a new precipitation sequence was proposed. To understand the effect of dislocations on the precipitates, the precipitation sequence in predeformed specimens were analyzed and compared with those in un-deformed conditions. It was found that the Q’ phase is more favorable to form in the presence of dislocations. The effect of precipitate types and morphologies on dislocation structures and orientation evolution were characterized by performing electron backscatter diffraction measurements on deformed specimens. The results showed that the density of geometrically necessary dislocations and their patterning are governed by the morphology of precipitates. Also, it was found that the
presence of peak-aged precipitates resulted in significant orientation spreading within the individual grains while this effect was less observed for over-aged precipitates. To understand the significance of interaction between precipitates and dislocations on the flow stress, the precipitate and dislocation structures parameters were characterized and the most important microstructural parameters were fitted into a phenomenological yield stress model. Experimental and statistical analysis showed a linear relationship between yield stress and average GND density. Based on the interaction of dislocations and precipitates, a rigorous micromechanical model for elastic-plastic deformation of crystals containing elastic inclusions was developed. The model is based on a novel method for calculation of elastic strain energy associated with incompatible deformation of matrix and inclusion, by representing it with the interaction energy of geometrically necessary dislocations. The resulting model is remarkably simple. It falls within the framework of classical crystal plasticity with a specific elastic-plastic constitutive law that accounts for shape of inclusions.
Table of Contents

Acknowledgments.............................................................................................................. iii
Abstract.............................................................................................................................. iv
List of Figures .................................................................................................................... ix
List of Tables ................................................................................................................... xiv
1. Introduction ..................................................................................................................... 1
  1.1 Multiscale Modeling of Materials............................................................................. 3
  1.2 Internal State Variable Modeling.............................................................................. 5
  1.3 Dislocation-Precipitation Interaction ......................................................................... 7
  1.4 Outline & Objectives of the Current Research ................................................................. 9
  1.5 References ................................................................................................................ 12
2. Characterization Techniques .......................................................................................... 13
  2.1 Introduction.................................................................................................................. 13
  2.2 Materials ................................................................................................................... 13
  2.3 Differential Scanning Calorimetry............................................................................. 14
  2.4 Scanning Electron Microscopy .................................................................................. 16
  2.5 Electron Backscattered Diffraction .......................................................................... 17
  2.6 Transmission Electron Microscopy ......................................................................... 19
  2.7 Energy Dispersive Spectroscopy ............................................................................. 21
  2.8 References ................................................................................................................ 22
3. Characterization of the Precipitation Sequence in AA6022 ......................................... 23
  3.1 Introduction.................................................................................................................. 23
  3.2 Background ............................................................................................................... 23
  3.3 Experimental Plan .................................................................................................... 25
  3.4 Results and Discussion ............................................................................................. 26
  3.5 Conclusions ............................................................................................................... 37
  3.6 References ................................................................................................................ 39
4. The Effect of Dislocations on Precipitates in AA6022...................................................... 40
  4.1 Introduction.................................................................................................................. 40
  4.2 Background ............................................................................................................... 40
  4.3 Experimental Plan .................................................................................................... 41
  4.4 Results....................................................................................................................... 42
  4.5 Discussion ................................................................................................................ 46
  4.6 Conclusions ............................................................................................................... 55
  4.7 References ................................................................................................................ 57
  5.1. Introduction .............................................................................................................. 59
List of Figures

Fig. 1.1) Schematic of important modeling aspects at each size scale for the casting example [6]. ................................................................. 5
Fig. 1.2) A schematic illustrating the interaction of dislocation line with precipitates [1]. 7
Fig 1.3) A dislocation pinned by the precipitates under applied stress will (a) bypass or (b) shear the precipitates [11]. ................................................................. 8
Fig. 2.1) A schematic of (a) DSC machine and (b) DSC curve; demonstrating the appearance of several common features in amorphous materials [1]......................... 15
Figure 2.2) (a) Schematic showing the formation of Kikuchi lines using EBSD in SEM, and (b) the projection of Kikuchi bands on the Phosphor screen [4]............................. 18
Fig 2.3) Two basic operation of the TEM imaging systems involve (A) projecting the diffraction pattern on the viewing screen and (b) projecting the image onto the screen [5]. .................................................................................. 20
Fig. 3.1) DSC trace of an as-quenched sample taken at a scan rate of 10°C/min............. 27
Fig. 3.2) TEM micrograph of precipitates in the <100> zone axes of aluminum. (a) specimen heated in the DSC until peak 3a; (b) specimen aged at 175°C for 30min........... 28
Fig. 3.3) DSC traces of AA6022 in as-quenched condition; (a) Immediately after quenching (b) Quenched and then one day stored at -5°C; (C) Quenched and stored 15 days at -5°C; Heating rate of 10°C/min................................................................. 29
Fig. 3.4) (a) Microstructure of specimen heated up to 270°C. (b) The magnified image of the region marked in (a). (c) The dark field image of the reflections shown in (d) shows the presence of lath-shaped and β'' precipitates. (d) The <100>Al SAD pattern of microstructure in (a). The key diagram for (d) is shown in (e) [12].................................................. 31
Fig. 3.5) (a) The microstructure of the sample heated up to 315°C with heating rate of 10°C/min. The precipitates are either β' or Q' and are marked by arrows. (b) The <100> Al zone axes TEM diffraction pattern of microstructure in (a), the (2131)γ and (0221)β spots are labeled in the diffraction pattern accordingly. (c) Schematic representation of the diffraction pattern in (b) [1]. The presence of extra symmetric spots in the experimental diffraction pattern is due to double diffraction. ......................... 33
Fig. 3.6) (a) The microstructure of the sample heated up to 400°C with heating rate of 10°C/min. The EDS analysis indicates that the precipitates are either (b) Si or (c) β. ...... 34
Fig. 3.7) The variation of hardness versus time for AA6022 during aging at 175°C....... 34
Fig. 3.8) (a) The microstructure of the sample aged 500min at 175°C. The majority of the precipitates are β'' and a few lath-shaped precipitates are marked in the magnified image (b). (c) The dark field image of the reflections marked in the <100> Al zone axes TEM diffraction (d). ................................................................. 35
Fig. 3.9) (a) The microstructure of the sample aged 300min at 175°C. (b) The SAD pattern in the <100> direction of Al zone axes suggests that the precipitates are β". (c)
The dark field image of the reflections indicated in (b) confirms that no lath-shaped precipitates are present...

Fig. 3.10) (a) The microstructure of the sample aged for 730 min at 175°C. According to the SAD pattern in the <100> direction of Al the majority of the precipitates are β". (c) Dark field imaging of the reflections indicated in (b) revealed the presence of a few β" rods.

Fig. 4.1) DSC traces of AA6022 (a) in the as quenched condition, (b) after 15% deformation and (c) after 30% deformation.

Fig. 4.2) (a) Bright field TEM micrograph, (b) the corresponding [001]Al diffraction pattern, the (2131)β and (0221)β spots are labeled in the diffraction pattern accordingly and (c) schematic representation of the diffraction of AA6022 deformed 30% and heated at a rate of 20°C/min to just beyond DSC peak 2" shown in Fig. 1c.

Fig. 4.3) Bright field TEM micrographs of AA6022 heated at a heating rate of 20°C/min to the end of DSC (a) peak 3, (b) peak 3' and (c) peak 3" shown in Fig. 4.1. (d) is the diffraction pattern corresponding to (c).

Fig. 4.4) β precipitation peaks in the as quenched alloy at 10°C/min, 15°C/min and 20°C/min heating rates.

Fig. 4.5) Plot after using equation (4) for calculating Q* and k0 based on assuming f(Y)=1-Y for β precipitation.

Fig. 4.6) Y2 (T) versus temperature for (a) peak 2 precipitation, (b) peak 2' precipitation (c) peak 2" precipitation.

Fig. 5.1) AA6022 samples aged at 175°C for (a) 500 min and (b) 5500 min.

Fig. 5.2) GND distribution plot for the samples aged (a) 500 min (b) 5500 min and then deformed 10% (c) GND density comparison for these two samples after 0 and 10% deformation.

Fig. 5.3) The orientation evolution in the overaged specimens; (a) after 0% deformation, and (b) after 20% deformation.

Fig. 5.4) The orientation evolution in peak-aged specimens; (a) after 0% deformation (b) after 20% deformation.

Fig. 6.1) Schematic showing the process of channel die deformation used in this study.

Fig. 6.2) Boundary maps showing well recovered microstructure after hot deformation for (a) 5005 and (b) 6022 Al alloys. Each line in the images represent misorientation of 1° or higher.

Fig. 6.3) Orientation images of (a) 5005 and (b) 6002 Al alloys after recrystallization treatment. The orientation shading key is shown at the right.

Fig. 6.4) Plot showing flow stress obtained during channel die compression as a function of Z for both 5005 and 6022 Al alloys.

Fig. 6.5) (001) texture pole figures of 6022 Al alloy showing predominantly cube texture for samples deformed under various processing conditions.
Fig. 6.6) (001) texture pole figures in 5005 Al alloy showing predominantly rotated cube texture for samples deformed under various processing conditions. .............................. 81

Fig. 6.7) Plot showing variation in % change in flow stress versus deformation conditions (described by Z * strain) for 5005 and 6022 Al alloys. .............................. 82

Fig. 6.8) Plot showing variation in 0.2% yield stress (MPa) obtained during tensile testing with square root of GND density (x108/m) for 6022 Al alloy. ......................... 83

Fig. 6.9) Stress-Strain curve of AA6022 for samples containing different GND densities in the starting microstructure. ................................................................. 84

Fig. 6.10) TEM image of deformed Ni showing geometrically necessary boundaries and incidental dislocation boundaries. ............................................................... 85

Fig. 6.11) Summary of regression analysis showing influence of microstructural parameters on the yield stress of 6022 Al alloy. ................................................................. 90

Fig. 7.1) Bright Field TEM micrograph of microstructure of hardening precipitates. (a) Al-Mg-Si alloys. Small needle-shaped β” precipitates are homogenously distributed in the matrix [7]. (b) Al-Cu alloys. The disk-shaped θ´ precipitates are seen in the microstructure [8]. ................................................................. 95

Fig. 7.2) (a) Schematic representation of the representative volume element with volume VRVE, (b) Cuboidal particle with volume of V ............................... 99

Fig. 7.3) (a) Application of the eigenstrain $\varepsilon_{11}^*$ in the particle. (b) Schematic representation of GN dislocation loops that are geometrically equivalent to eigenstrain $\varepsilon_{11}^*$ ................................................................. 103

Fig. 7.4) (a) Application of the eigenstrain $\varepsilon_{12}^*$ in the particle. (b) Schematic representation of GN dislocation loops that are geometrically equivalent to eigenstrain $\varepsilon_{12}^*$ ............................... 104

Fig. 7.5) Schematic representation of GN dislocation loops that are geometrically equivalent to eigenstrains $\varepsilon_{11}^*$ and $\varepsilon_{23}^*$ ................................................................. 105

Fig. 7.6) The schematic diagram of a Nye’s dislocation density component representing a pile-up of dislocations. (a) The boundary layer thickness, $\lambda$, is small relative to the particle thickness, L. (b) The boundary layer consisting of dislocations piled-up against a thin particle, $\lambda/L \geq 1$. ................................................................. 110

Fig. 8.1) (a) Hemming process of AA6022 sheet; (b) formation of cracks in AA6022 after bending [1]. ................................................................. 116

Fig. B.1) Experimental configuration used for shock-loading and soft recovery of aluminum samples shocked to about 2.3 GPa. The inside of the soft recover fixture was filled with absorbent materials to minimize secondary loading of the recovered aluminum sample after impact and release from the guard ring. ................................................................. 132

Fig. B.2) DSC thermogram of the as-quenched sample taken at a heating rate of 10°C/min. ................................................................. 135
Fig. B.3) Microstructure of specimen heated up to 230°C. (a) The needle shaped β" precipitates+ Lath shaped precipitates. (b) The <100>Al SAD pattern of microstructure in (a) ................................................................. 136

Fig. B.4) (a) The microstructure of the sample heated to 275°C with heating rate of 10°C/min. The precipitates are either β' or Q' and are shown by arrows. (b) The <100> Al zone axes TEM diffraction pattern of microstructure (a) and its analyses (c)............. 138

Fig. B.5) (a)The microstructure of the sample heated to 315°C with heating rate of 10°C/min. The EDS analysis indicates that the precipitates are (b) Si and (c) β. (d) <100>Al diffraction pattern corresponds to microstructure (a). (e) Schematic of the diffraction pattern (d)........................................................................ 139

Fig. B.6) DSC curves at a heating rate of 10°C/min for samples (a) as-quenched condition (b) shock-loaded prior to DSC run. ................................................................. 141

Fig. B.7) The microstructure of the sample shock-loaded prior to DSC heating experiment after the occurrence of peak II’ (a) Bright field imaging (b) SAD pattern at <100>Al zone axes. ...................................................... 142

Fig. B.8) The microstructure of the sample shock-loaded prior to the DSC heating experiment after the occurrence of peak III’ (a) Bright field imaging (b) SAD pattern at <100>Al zone axes. ........................................................................................................ 144

Fig. B.9) The <100>Al TEM dark field micrograph of the microstructure of shock-loaded sample after the occurrence of peak III’. .............................................................. 144

Fig. B.10) The microstructure of shock-loaded sample heated to peak IV’ (~330°C) (a) The dark field micrograph shows β-cubes (b) The diffraction pattern including <100>β-cubes and <100>Al (c) The schematic representation of (b)............................. 145

Fig. B.11) Dependence of hardness on artificial aging time at 175°C. (a) without shock-loading (b) with shock-loading. ...................................................................................... 146

Fig. B.12) The microstructure of AA6022 after being quenched from solutionizing temperature and subsequently shock-loaded to 23 GPa. ...................................................... 147

Fig. B.13) Bright field imaging and SAD pattern at <100>Al zone axes of the microstructure of the AA6022 aged at 175°C for 500min (a-b) without shock (c-d) with shock. ........................................................................ 148

Fig. C.1) Artificial Neural Network Architecture............................................................. 157

Fig. C.2) Variation of hardness versus time for AA6022 during aging at 175°C. ........... 165

Fig. C.3) TEM dark field images of precipitates after aging at 175°C for (a) 140min, (b) 500min, (c) 730min and (d) 5500min................................................................. 166

Fig. C.4) TEM enhanced images for (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C................................................................. 167

Fig. C.5) FFT filtering (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C, the inset is the FFT pattern................................. 168

Fig. C.6) Precipitates Area distribution (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C................................................................. 170
Fig. C.7) Rose figures for Nearest Neighborhood Direction (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175ºC................................................................. 171

Fig. C.8) Nearest Neighborhood Distance (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175ºC................................................................. 173

Fig. C.9) Major axis to minor axis ratio (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175ºC................................................................. 174

Fig. C.10) Model output for data used in training, the inset is the error curve............ 176

Fig. C.11) MSE of ANN model output versus number of neurons (50 epochs).......... 177

Fig. C.12) MSE of ANN model output versus number of epochs (25 neurons in the hidden layer). ................................................................. 177

Fig. C.13) (a) The orientation relationship of rod-like precipitates in the unit crystal of aluminum matrix. The precipitates are oriented in <100> direction of aluminum. (b) The interaction of rod-like precipitates with dislocations in {111} plane. (c) The orientation relationship of lath-shaped precipitates in the unit crystal of aluminum matrix. The precipitates are oriented in <100> direction of aluminum. (b) The interaction of lath-shaped precipitates with dislocations in {111} plane. The shadowed triangle represents the {111} plane. ................................................................. 180

Fig. C.14) TEM dark field images of precipitates in a deformed sample after aging at 175ºC for 480mins................................................................. 183
List of Tables

Table 2.1) Chemical compositions (in wt. %) of 5005 and 6022 Al alloys................. 14
Table 4.1) Analysis of the DSC curve in Fig. 4.1a...................................................... 43
Table 4.2) Measured activation energy and k0 values for peaks 2, 2΄ and 2˝ precipitation indicated in Fig. 4.1 ................................................................. 50
Table 6.1) Different combinations of processing parameters used in the study.......... 72
Table C.1) The average influence of inputs on the model after multiple program runs. 178
Table C.2) Model prediction for data taken at 500mins and 140mins......................... 181
Dedication

This dissertation is dedicated to my mother, father and two sisters who provided both emotional and financial support
Chapter 1

1. Introduction

A large number of constitutive equations describing the plastic behavior of materials are available for materials modeling applications. At the same time, the material modeling is crucial for obtaining accurate results in simulations of manufacturing processes. However, the applicability of commonly used constitutive equations is usually limited in terms of both processing parameters including strain, strain rate and temperature, and the evolution of microstructural features including dislocation structures, precipitate morphologies, grain orientations, and grain size and their shape. It is possible in general to trial different spatial and temporal discretizations in order to reduce the error due to these factors in the simulation process. However, errors in the material model or in the pertinent parameters cannot be reduced by numerical procedures, and so the problem of modeling material behavior is most challenging step in materials models.

According to Ashby [1], material models can be divided into two major groups. *Engineering or empirical* models are determined by means of fitting model equations and parameters with experimental data without considering the physical processes causing the observed behavior. These empirical models are also named engineering models as they are more common in engineering applications than the physically based material models. *Physically based* material models, on the other hand, are models where knowledge about the underlying physical process, dislocation processes etc, is used to formulate the constitutive equations. Naturally, the division between these kinds of models is somewhat arbitrarily. In any case, the formulated model must be consistent with the principles of
thermodynamics. Based on the consideration of the underlying physical processes, the physically based models are expected to have a larger range of usability and validity than more commonly used empirical models. As can be seen in the literature, there has been some progress made to model the evolution of the microstructure for some limited processes but it is not expected that it will be possible to find one universal model covering all aspects of the behavior of a given material [2].

Since a material deformation behavior is a function of its history, a crucial aspect of the modeling is to understand the microstructure-property relations. One successful method of capturing history effects in inelastic material through computational modeling of the manufacturing and in-service life cycle is through the use of internal state variable theory. The internal state variable approaches include the microstructure-property relations that can be coupled with the ‘multiscale modeling’ effort to establish a multiscale physically based model.

To successfully achieve the multiscale physically based modeling of materials, one has to have a good understanding of structural evolutions during materials processing. Structural evolution means that the structure, and thus the behavior of the material, evolves with time. However, modeling the structural evolutions is not an easy task due to our lack of knowledge about the exact mechanisms which result in structural evolution. Moreover, materials behavior frequently involves further levels of complexity because of multiple mechanisms and linked processes. The grain growth during sintering of crystalline powders, growth of voids during deformation, and interaction of precipitation and dislocations are a few examples of structural evolution. In precipitation hardening materials the interaction of precipitation-dislocations plays an important role in
governing the materials behavior and thus the work in this thesis is devoted to investigate this interaction in more details.

The sections of this chapter are organized as below. In Sections 1.1 and 1.2 the fundamentals of multiscale modeling and internal state variable modeling will be briefly explained. Since the focus of this dissertation is on the interaction between precipitates and dislocations and thus in Section 1.3, a brief review on experimental characterization and theoretical modeling of this interaction will be discussed. These sections will be followed by Section 1.4 which describes the outline and objectives of the each chapter of the current dissertation.

1.1 Multiscale Modeling of Materials

Generally, the levels of the description of material behavior can be divided into nano-(atomistic level), micro- (dislocations and unit voids and inclusions), meso- (larger part of a microstructure of material, i.e. combinations of many inclusions, layers, gradients) and macrolevel (specimen). Multiscale modeling is vertically oriented employing different computational methods at each length scale to determine the cause and effect microstructure-property relations for use at the next higher level. Experiments are performed at the next higher level for two purposes: to validate the lower scale cause and effect relations and to help determine the next level effects to be pushed up the next level. Techniques are being developed in which numerical methods are used to bridge the gap. For example, Shenoy et al. [3] have connected atomistics to finite element methods. Hughes et al. [4] have developed a finite element scheme to admit microstructures at a fine scale and other microstructural features at the coarse scale. Moorthy and Ghosh [5]
have used Voronoi tessellation techniques to capture geometric affects in the microstructure. This methodology presents a clear path for integrating research into practical engineering problems.

The path to connect different scales and establish a multiscale model are can be reviewed by an example illustrated in Figure 1.1 which shows the important features and size scales that were pertinent at each size scale for the cast A356 aluminum alloy used as a control arm in automotive applications [6]. In the atomistic scale, ab initio calculations were performed in order to develop a Modified Embedded Atom Method (MEAM) potential for the aluminum silicon system. Once the potential was developed, MEAM simulations were performed to determine the conditions when silicon fracture would occur versus silicon-interface debonding. In the micron size scale finite element analyses focused on the void crack nucleation progression while in the Mesoscale I analysis (1–200 microns), the focus was on pores arising from silicon fracture and interface debonding. The Mesoscale II finite element simulations (200–500 microns) focused on pore-pore interactions to give insight into coalescence from casting porosity. Eventually the simulations in the structural scales accurately predicted the final failure locations of the control arm and validated with experimental investigations.
1.2 Internal State Variable Modeling

The internal state variable (ISV) formulation first laid out by Coleman and Gurtin [7] and later enhanced by Rice [8], relates the internal state variables to microstructural characteristics and has been used in various materials: composites, polymers, and ceramics. The ISV formulation is a means to capture the effects of a representative volume element but not all of the complex causes at the local level; hence, an ISV will macroscopically average in some fashion the details of the microscopic arrangement. In essence, the complete microstructural arrangement is unnecessary as long as the macroscale ISV representation is complete [9]. As a result, the ISV must be based on physically observed behavior and constrained by the laws of thermodynamics.
The ISV formulation has been used to describe a variety of materials behavior including non-isothermal transformation and deformation behavior of steels and aluminum alloys. This formulation consists of evolution equations for the microstructural elements and a state equation which connects the microstructural parameters to the materials behavior. The generalized constitutive equation for the flow stress response during thermomechanical processing of Al alloys can be written in the form [10]:

\[
\sigma = F(\dot{\varepsilon}, T, S_i)
\]

where \(\sigma\) is the effective true stress, \(\dot{\varepsilon}\) is the effective true strain rate, \(T\) is temperature and \(S_i\) are the internal state variables which accounts for the influence of the microstructure on the flow stress. In aluminum alloys, \(S_i\) parameters are representing chemistry, dislocation structure, particle morphology, etc. The rate of the microstructural evolution is influenced by the externally imposed variables including temperature and strain rate, and the current state of the microstructure itself. The evolution of the microstructural parameters is related by a set of kinetic equations as follows:

\[
\dot{S}_i = (\dot{\varepsilon}, T, S)
\]

In this dissertation the first phase in constitutive model development was to identify the minimum number of microstructural variables necessary to adequately account for the influence of the changes in microstructure to the flow stress. To accomplish this, statistical based approaches were used to analyze the effect of microstructural parameters and identifying the most effective variable on the materials response.
1.3 Dislocation-Precipitation Interaction

One of the classical fields in physical metallurgy is the interactions between dislocations and precipitates which is usually divided in several areas of research; (i) precipitation on dislocations, and more generally heterogeneous precipitation on structural defects (including also sub-grain boundaries, grain boundaries and dispersoids); (ii) movement of dislocations through an array of precipitates (Fig. 1.2), and the resulting mechanical properties (yield stress and work hardening rate). Precipitation hardening aluminum alloys undergo complicated processing routes in which all of these processes occur concomitantly, so that a complete understanding of the final microstructure and its relation to the mechanical properties requires an overall view of all these types of interactions.

The movement of dislocations in precipitation hardening materials strongly depends on the morphology of particles in the matrix such as size distribution, inter-particle spacing, shape of particles and volume fraction. Figure 1.3 shows an example of the effect of precipitate morphology on dislocation motion. During the interaction process
A dislocation pinned by the precipitates under applied stress will bypass or shear the precipitates. The parameters determining the deformation mechanisms are essentially the precipitate characteristics: shape, size, density, structure, composition and the precipitate/matrix orientation relationships. Unfortunately, most of them are unknown for alloys of commercial interest since property optimization leads to numerous solute additions and to supersaturated solid solution exhibiting complex precipitation sequences.

Fig 1.3) A dislocation pinned by the precipitates under applied stress will (a) bypass or (b) shear the precipitates [11].

In order to define the importance and the contribution of this work in the literature, it is worth briefly reviewing the experimental characterization and modeling efforts on describing the precipitation-dislocation interactions. Experimental investigations on precipitation hardening materials indicate that the plastic behavior and mechanical properties are influenced by the presence of particles (eg, [12-14]). It has been noticed that while precipitates can influence the initial yield strength and its
anisotropy, they can also dominate the hardening behavior of the material. Several mechanical models related to these hardening effects have been suggested in the literature [12,13, 15-20]. However rare results are available concerning a general continuum micromechanics formulation for the elastoplastic behavior of materials containing hardening particles in the framework of crystal plasticity. One of the first few attempts to represent the elastoplastic behavior of these materials in crystal plasticity formulation was made by Schmitt et al [16]. He represented the crystal plasticity framework for the single crystals containing non-shearable particles in the infinitesimal strain formulation. Latter on this model was extended to polycrystals by Bonfoh et al [18]. Recently Han et al [19,20] have suggested a crystal plasticity description for the materials containing hardening particles but fail to consider the effect of the particles on hardening of the material.

For alloys containing hardening precipitates, it appears to be more realistic to consider that the precipitates modify the critical shear stress on slip systems and in this way change the single crystal constitutive relation. Thus, the modeling effort of this work is to derive this constitutive rule for single crystal containing hardening precipitates considering the interaction between precipitates and dislocations.

1.4 Outline & Objectives of the Current Research

The current dissertation aims to provide a fundamental understanding of the interaction between precipitates and dislocations and to illustrate this by reference to the precipitation hardening Al alloys, specifically 6xxx series. Following are the outline and general objectives of the current research:
a. Chapter 2 illustrates the experimental techniques that were used to characterize the precipitation and dislocation interactions. These techniques include transmission electron microscopy, electron backscatter diffraction, scanning electron microscopy, differential scanning calorimetry, and energy dispersive spectroscopy.

b. In Chapter 3, different types of precipitate structures and morphologies in the material subjected to the current analyses were characterized and the precipitation sequence was identified.

c. Chapters 4 and 5 describe the effect of dislocation structure on the precipitation behavior and the effect of precipitate morphologies on dislocation structures respectively.

d. Chapter 6 deals with identifying the most important microstructural parameter affecting the behavior of 5005 and 6022 Al alloys. To accomplish this, a series hot deformation experiments were performed to produce various precipitate morphologies and dislocation structures. A statistical formulation was used to identify important microstructural parameters that influence the yield stress of 6022 alloy and yield strength model was developed as a function of microstructural parameters.

e. In Chapter 7, a micromechanical model connecting discrete dislocation mechanics to the continuum mechanics in the framework of crystal plasticity is developed to account for interaction of geometrically necessary dislocations with precipitates.

f. Chapter 8 describes the overall contribution of the current research and its significance.
g. Chapter 9 describes the main conclusions of the current dissertation.

h. Chapter 10 contains suggestions for future work.
1.5 References


Chapter 2

2. Characterization Techniques

2.1 Introduction

To capture the applicable ISV microstructure-property relations, material characterization coupled with mechanical property tests are required. Characterization techniques such as scanning electron microscope, transmission electron microscope, and electron backscattered diffraction have revealed great promise in capturing microstructural states and their correlated rates. In this chapter a brief review on the materials and characterization techniques that have been used in this dissertation will be given to assist the readers with better understanding of the subsequent chapters.

2.2 Materials

Two aluminum alloys: a heat treatable alloy, 6022, and a non-heat treatable alloy, 5005, were examined in the current research project. The composition of these two alloys is given in Table 2.1. The 6022 aluminum alloy (AA6022) can be strengthened by the precipitation of second phases, while AA5005 does not show effective precipitation hardening. Since the focus of this dissertation is on the interaction of precipitates with dislocations, the majority of characterizations were conducted on AA6022. The microstructure of AA5005 was studied in Chapter 7 and compared with those in AA6022.
Table 2.1) Chemical compositions (in wt. %) of 5005 and 6022 Al alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Cu</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>5005</td>
<td>0.7-1.1</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>6022</td>
<td>0.55</td>
<td>0.056</td>
<td>1.1</td>
</tr>
</tbody>
</table>

2.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate [1]. In DSC, the sample and reference are connected by a low resistance heat flow path (a metal disc). The assembly is enclosed in a single furnace. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is exothermic or endothermic. Differential scanning calorimetry can be used to measure a number of characteristic parameters of a sample. Using this technique it is possible to observe fusion, phase transformations, crystallization events, glass transition temperatures ($T_g$), and chemical reactions.
Fig. 2.1) A schematic of (a) DSC machine and (b) DSC curve; demonstrating the appearance of several common features in amorphous materials [1].

In this research project, a SP DSC-Rheometric Scientific™ instrument was used for calorimetric analyses. It is necessary to calibrate the DSC set up before conducting the real experiments. Three types of calibrations including temperature calibration, furnace calibration and sensitivity calibration were performed using standard samples including Tin, Zn, Pb, and Sapphire specimens. A protective atmosphere of pure Argon at the rate of 11 ml/min was passed through the cell to avoid oxidation. The system consisted of two cells which contained two aluminum pans. One of the pans was used for
the reference and the other was used for the sample with similar weight. The output was in mW and the net heat flow of the reference material relative to the sample was recorded as a function temperature. Discs of high purity (99.9999%) aluminum annealed at 520°C and cooled in the furnace to room temperature were used as the reference. To isolate the heat effects due to reactions occurring in the alloy, the curve obtained from Pure Al- Pure Al run was used as a baseline and subtracted from the Al alloy- Pure Al data.

### 2.4 Scanning Electron Microscopy

In scanning electron microscopy (SEM) an electron beam is focused and scanned across the surface of specimen. When the electrons hit the specimen, a variety of signals is generated due to the interaction of a primary electron with matter [2]. Every signal recorded by one of the detectors gives specific information of the sampled volume of the specimen or its chemical content. The most common imaging mode, secondary electron imaging (SEI), monitors low energy (~<50 eV) secondary electrons. Due to their low energy, these electrons must originate within a few tenths of a nanometer from the surface. In addition to the secondary electrons, backscattered electrons (essentially elastically scattered primary electrons) can also be detected and used for imaging (BSI).

In this research project, both BSI and SEI were used to characterize the morphology of precipitate structure. This information was analyzed in Chapter 6. SEI and BSI was performed in Alcoa Technical Center with a Field Emission SEM (FESEM) at operating voltage of 20KeV and 5KeV respectively.
2.5 Electron Backscattered Diffraction

Electron backscatter diffraction (EBSD) is one of the most exciting techniques in scanning electron microscopy. EBSD can be used to examine a wide range of crystalline materials and to measure microstructure, orientation, texture (microtexture) and boundary properties. It can also be used in conjunction with chemical analyses to identify unknown phases. In this technique an electron diffraction pattern is formed by coherently backscattered electrons diffracted by planes matching the Bragg condition [3],

\[ \lambda = 2d \sin \theta \]  

(2.1)

where \( \lambda \) is the wavelength of the electron beam, \( d \) is the interplanar spacing for a given set of lattice planes and \( \theta \) is the Bragg angle. The collection of an electron backscatter diffraction pattern (EBSP) in the SEM is relatively straightforward. A polished sample must be tilted to a relatively high angle (typically 70°) inside the SEM. When an electron beam encounters a solid material, it is inelastically scattered in all directions beneath the surface of the material (Fig. 2.2a). Because the electrons travel from the source in all directions, for each set planes for which the Bragg condition is satisfied, the diffracted beams lie on the surface of a cone whose axis is normal to the diffracted plane. Those cones intersect with a phosphor screen placed in front of the specimen and give rise to the pattern (Fig. 2.2b). Each pair of cones, whose intersection with the phosphor screen produces a nearly parallel set of lines, is termed a Kikuchi band. An image analysis technique, called Hough transform (modified Radon transform) is used to detect Kikuchi bands. The Hough transform is given by \( \rho = x \cos \sigma + y \sin \sigma \), which integrates intensity along all possible straight lines, reducing all lines in real space to a single point defined by \((\rho, \sigma)\) in Hough space. Usually automated indexing of EBSD patterns is done using
sophisticated software algorithms. One major advantage of the EBSD technique is that measurements can be performed on a large area of the sample and thus statistically reliable orientation information can be obtained. Resolution of the technique is dependent upon the SEM type and atomic number of the metal. Typically under best conditions, an angular resolution in modern FEG-SEM instruments is about 0.5° and spatial resolution is 20 nm.

Figure 2.2) (a) Schematic showing the formation of Kikuchi lines using EBSD in SEM, and (b) the projection of Kikuchi bands on the Phosphor screen [4].

In this research work, the surface of mechanically polished samples was studied using electron back scattered diffraction system attached to the W-filament CamScan SEM and a LaB6-filament JEOL 6400 SEM. The high resolution EBSD data (step size of 0.2µm) was collected at Alcoa Technical Center using a Philips XL30 FESEM operating at voltage of 20KeV. OIM Data Collection 4.0 was used for acquiring EBSD data in the SEM. Then EBSD data were analyzed with Orientation Imaging Microscopy (OIM) software version 4.0.
2.6 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an imaging technique whereby a relatively thin specimen is hit by the high energy electrons introducing numerous interactions [5]. One of the greatest advantages of the TEM is the excellent resolution due to short wavelength of electrons (approximately 0.0025nm at 200KeV). However, the resolution is limited by the relatively poor performance of the electromagnetic lens systems, particularly by the spherical aberration Cs.

Diffraction mode and image mode are the two widely used methods of specimen observation obtained by TEM (Fig 2.3). An image in TEM is mainly formed by elastically scattered electrons. These scattered electrons result in scattered beams that are, together with the transmitted beam, projected on the fluorescent screen. The image contrast can easily be enhanced by using only the transmitted beam and blocking the scattered beams making use of the objective aperture. This type of imaging is called bright field (BF) imaging. If instead of transmitted beam, the diffracted electrons are used for imaging it is called dark field (DF) imaging. In diffraction mode, a spot pattern of an illuminated area will be obtained which can be used to identify the crystallography of that area.
Fig 2.3) Two basic operation of the TEM imaging systems involve (A) projecting the diffraction pattern on the viewing screen and (b) projecting the image onto the screen [5].

In this research work, a CM 200 Philips microscope operated at 200 KeV and a Philips TM420 microscope are used to identify the precipitation sequence and to investigate the precipitate morphologies in 6022 aluminum alloy. TEM specimens prepared by twin jet polishing in solution of 30% HNO3 and 70% Methanol at ~20°C.
2.7 Energy Dispersive Spectroscopy

The Energy Dispersive X-ray Spectroscopy (EDS) technique is based on the characteristic X-rays that are generated when an electron beam interacts with the specimen [2]. The incident electrons may interact with the electrons within matter, present in for instance the K-shell of the atoms. The electron in this shell might be ejected, when a critical amount of energy is transferred, leaving the atom in an ionized state. The characteristic x-rays are generated as an electron out of the L or M shell fills this vacancy. The energies between these shells are specific for each element. Therefore, capturing the energy of the characteristic X-rays allows identification of the illuminated element. The characteristic X-rays produced, can be captured by the EDS detector within a discrete time interval. The number of counts per second (CPS) and dead time (DT), the time when detector processes a X-ray signal, should be sufficient to reach an acceptable signal to noise ratio.

In this dissertation the EDS systems (manufactured by EDAX Inc.) attached to both SEM and TEM were used to identify the chemical composition of precipitates. In SEM analysis, the working distance was set to 15mm, and the beam current and aperture size were properly adjusted to result in 10,000 to 20,000 CPS and a DT between 10% to 30%. In TEM analysis, the objective aperture was removed and spot size of 3 or 4 were used to obtain the spectrum with CPS and DT similar to SEM measurements.
2.8 References


Chapter 3

3. Characterization of the Precipitation Sequence in AA6022

3.1 Introduction

To study the interaction of precipitation and dislocations, it is important to have a good understanding about the morphology and precipitate types which may exist in the material. Although the precipitation reactions in Al-Mg-Si alloys have been studied extensively, details of the precipitation sequence in aluminum alloy 6022 have not yet been fully understood. The objective of this chapter is to identify the precipitates and their sequence in AA6022. Differential scanning calorimetry and transmission electron microscopy were used to characterize the precipitation reactions in this alloy. It was observed that in the early stages of aging there are some small precipitates which form prior to the formation of $\beta''$ precipitates. Studies on isothermally aged and DSC heated samples suggest that some of the $\beta''$ needles transform during growth to lath-shaped precipitates. An alternative precipitation sequence for AA6022 is also proposed.

3.2 Background

Heat treatable Al-Mg-Si alloys have been used in the automotive and construction industries due to their combination of forming characteristics and final mechanical properties. AA6022 is an important member in the family of Al-Mg-Si alloys and was developed in 1995 for use as automotive sheet panel. In body panel sheet materials two important properties need to be optimized, the formability and the strength. It has been found that the paint bake process plays a key role in optimizing these properties. In this
process the solution treated alloy is baked at a temperature of 175°C, and thus the precipitation sequence needs to be understood better to optimize the process. Recently Miao and Laughlin [1,2] studied the precipitation sequence in 6022 aluminum alloy and they proposed the following reaction:

\[
\text{solid solution } \alpha \rightarrow \text{GP zones} \rightarrow \beta' \rightarrow \beta + \text{lath-like precipitates} \rightarrow \beta + \text{Si}
\]

Studies assisted by high resolution transmission electron microscopy (HRTEM) and atomic probe field ion microscopy (APFIM) show that GP zones in Al-Mg-Si alloys are spherical clusters and are fully coherent with the matrix [1,3-5]. The \(\beta'\) precipitates are fine needle-shaped precipitates along \(<100>_{\text{Al}}\) with a C-centered monoclinic structure [3-6]. The \(\beta\) precipitates are reported to be rod-like precipitates along \(<100>_{\text{Al}}\), and have a hexagonal crystal structure with \(a = 0.705\) nm and \(c = 0.405\) nm [6]. The structure and composition of the \(\beta\) phase has been established to be of the fluorite structure with a composition of Mg$_5$Si [7]. The lath-shaped precipitates are believed to be one of Q phase precursors and have been denoted as Q' [1,2]. Both Q and Q' phase have hexagonal crystal structure with lattice parameter of \(a=1.04\)nm and \(c=0.405\)nm [8] and several chemical compositions of the phase have been reported (e.g. Al$_4$Cu$_2$Mg$_8$Si$_7$ [9]). The only difference between Q and Q' appears to be the degree of coherency of the phase with the matrix [8].

During body panel processing, AA6022 is isothermally aged at 175°C for 30 min prior to subsequent deformation process. However, the lack of formability of this alloy is one of the major issues during the body panel manufacturing, especially the bending
process. It is well accepted that in hardening aluminum alloys the formability highly depends on precipitate types and their morphologies. Therefore, this chapter aims to describe the precipitation sequence of AA6022 in more detail. Differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) were used to characterize the precipitation reactions in this alloy. Our results show some differences from the previous precipitation sequence proposed by Miao and Laughlin [1,2].

3.3 Experimental Plan

The as-received AA6022 specimens were thinned to 0.5 mm by mechanical polishing and punched to form 3 mm diameter disks prior to the DSC experiments. The average weight of the DSC samples was 9.4±0.3 mg. Prior to the DSC experiments, the samples were solution treated in a batch type furnace at 550ºC for 3 hours and water quenched to room temperature. The Rheometric Scientific™ DSC instrument was used for calorimetric analyses. A protective atmosphere of pure Argon at the rate of 11 ml/min was passed through the cell to avoid extensive oxidation during the experiment. All specimens were subjected to a heating rate of 10°C/min up to 550ºC. This procedure was repeated for several samples and good agreement in the plotted DSC curves was observed.

To characterize the microstructural evolution during the DSC tests, samples for TEM analyses were prepared by heating in the differential scanning calorimeter with the same heating profile used during the DSC experiments. Samples were removed from the DSC apparatus and immediately quenched in liquid nitrogen subsequent to achieving the temperature at which each peak in the DSC curves was observed. The time interval prior
to quenching was less than 3 sec. The samples were thinned to 150 µm by mechanical
polishing and punched in 3 mm disks prior to TEM imaging.

To study the precipitate evolution during isothermal aging, the as-received
specimens were solution treated at 550°C for 3 hours and subsequently water quenched to
room temperature. Then the samples were aged at 175°C in a salt bath furnace for various
periods of time. Vickers micro-hardness and TEM studies were performed on the aged
samples.

TEM specimens were electro-polished in a solution of 300 ml 69% nitric acid +
700 ml methanol at a temperature of -20°C ± 5°C by using a twin jet electro-polishing
unit. TEM investigations were carried out in a Philips TM420 microscope operating at
120KeV.

3.4 Results and Discussion

Figure 3.1 shows the typical DSC thermogram for the as-quenched material,
heated up to 550°C with a heating rate of 10°C/min. Five exothermic and one
endothermic peaks are seen in the DSC and marked by numbers along the curve.
Fig. 3.1) DSC trace of an as-quenched sample taken at a scan rate of 10°C/min.

The TEM studies on samples heated just above peak 1 and 2 did not show any contrast in bright field imaging and no pattern due to precipitates was found in selected area diffraction (SAD) patterns. Edwards et al [3], Murayama et al [4] and Dutta et al [5] have investigated extensively the nature of early stages of precipitation in Al-Mg-Si alloys by means of Atomic Probe Field Ion Microscopy (APFIM), and high resolution microscopy. Their results show that these exothermic peaks are related to the clustering of Mg/Si atoms and the formation of GP zones. Due to the blocky shape of the GP zones in Al-Mg-Si alloys, streaking from GP zones would not be expected to occur in diffraction pattern analyses. In addition, the atomic scattering factors of these three elements are very close to each other. Therefore it is difficult to resolve these zones by
conventional TEM imaging. Thus following the literature, peak 1 and peak 2 were characterized as clustering and GP zones.

![TEM micrograph](image)

Fig. 3.2) TEM micrograph of precipitates in the <100> zone axes of aluminum. (a) specimen heated in the DSC until peak 3a; (b) specimen aged at 175°C for 30min.

Figure 3.2a shows the precipitates in the sample heated up to 240°C. The SAD pattern of the sample contains no extra reflections for the precipitates and thus it suggests that the precipitates do not have any distinct structure. Although, these precipitates have been the center of focus by some researchers, their crystal structure and composition are still unclear [3, 10, 11]. These precipitates were suggested to be sensitive to Si content since they were observed in the Al-Mg-Si alloys with excessive silicon content [11]. The activation energy required for the formation of these precipitates was calculated by Bryant [10] to be around 92KJ/mole. By comparing this value with the activation energy for the diffusion of Mg (136KJ/mole) and Si (142KJ/mole), one may conclude that these precipitates can not be due to the migration of solute atoms. Bryant [10] observed these precipitates only in quenched and immediately heated samples. Our DSC experiments on the specimens which were quenched and kept at low temperatures (~ -5°C) for 1 day and 15 days (Figs. 3.3b and c) show that peak 3a disappeared for the specimens stored at low
temperatures in comparison to the one plotted immediately after quenching (Fig. 3.3a). This indicates that the rate of the formation of these precipitates is very fast. Therefore the mechanism of vacancy assisted migration of solutes for the formation of these precipitates, which was proposed by Bryant [10], seems to be reasonable. It should be mentioned that peak 3b is also shifted to higher temperatures (~10°C) in the low-temperature aged samples. This may be explained by the possible heterogeneous nucleation of peak 3b precipitates on peak 3a precipitates. In this case, the disappearance of peak 3a precipitates will result in retardation of the peak 3b precipitation kinetics.

Fig. 3.3) DSC traces of AA6022 in as-quenched condition; (a) Immediately after quenching (b) Quenched and then one day stored at -5°C; (C) Quenched and stored 15 days at -5°C; Heating rate of 10°C/min.
Figure 3.4 shows the TEM micrographs and SAD pattern of the alloy heated in the DSC apparatus to peak 3b in Fig. 3.1. The needle-shaped precipitates are distributed homogeneously in the matrix and their long axis is parallel to $<100>_{\text{Al}}$ and the dark spots are needles pointing in the viewing direction (Fig. 3.4a). The streaks seen in the diffraction pattern of Fig. 3.4d agree well with the schematic diffraction pattern for $\beta''$ proposed by Jacobs [12] which is shown in Fig. 4e. The SAD pattern is also identical to those reported by Murayama et al [3] and Edwards et al [4]. This indicates that DSC peak 3b corresponds to the formation of $\beta''$ precipitates. Close examination of the end-on precipitates shows that in addition to the needle-shaped precipitates, small lath-shaped precipitates are also present and it is shown at higher magnification in Fig. 3.4b. Dark field images (Fig. 3.4c) taken with the precipitate reflections (indicated in Fig. 3.4d) clearly show the presence of these lath-shaped precipitates. The lath-shaped precipitates are oriented at an angle of about 11° or less to $<100>_{\text{Al}}$ zone axes. This agrees well with characteristics of the $Q'$ precipitates. According to Chakrabarti and Laughlin [8] the habit plane and orientation relations of the lath-shaped precipitates at the late stage of overaging resembled that of $Q'$, while they were different for the lath-shaped precipitates at an early stage, thus indicating that they were possible precursors to the $Q'$ phase.
Fig. 3.4) (a) Microstructure of specimen heated up to 270°C. (b) The magnified image of the region marked in (a). (c) The dark field image of the reflections shown in (d) shows the presence of lath-shaped and β˝ precipitates. (d) The <100>Al SAD pattern of microstructure in (a). The key diagram for (d) is shown in (e) [12].

Figure 3.5a shows the bright field image of the precipitates after the occurrence of peak 4. The diffraction pattern (Fig. 3.5b) and its analyses (Fig. 3.5c) of the end-on precipitates in bright field TEM image (Fig. 3.5a) revealed the existence of two types of
precipitates, the lath-shaped and the rod-like $\beta'$ precipitates. The lath-shaped precipitates have an angle less than $11^\circ$ with the nearest $<100>_{\text{Al}}$ zone axis which is characteristic of the $Q'$ precipitates. The presence of $Q'$ in this alloy agrees well with the proposed phase diagram for Al-Mg-Si-Cu alloys [8]. Therefore one can expect that a metastable form of $Q$ (like $Q'$) is present in the precipitate sequence of the alloy. The energy dispersive spectrometry (EDS) analysis of precipitates on peak 5 (Fig. 3.6a) determined that they are either Si or Mg$_2$Si (Fig. 3.6b and c), but it was very difficult to distinguish them from each other on the basis of morphology.

Figure 3.7 shows the variation of Vickers microhardness of the alloy during aging at 175°C. Dark contrast arising from extremely fine particles is observed in Fig. 3.2b. The shape of the fine precipitates is not well defined since they are very fine (~2nm), and the SAD pattern shows neither extra reflections nor diffuse scattering, which suggests that the precipitates are fully coherent with the matrix and do not have distinct structure. Similar precipitate morphology was observed for the sample heated to 240°C in the DSC (Fig. 3.2a).
Fig. 3.5) (a) The microstructure of the sample heated up to 315°C with heating rate of 10°C/min. The precipitates are either β’ or Q’ and are marked by arrows. (b) The <100> Al zone axes TEM diffraction pattern of microstructure in (a), the (2131)Q' and (022)β’ spots are labeled in the diffraction pattern accordingly. (c) Schematic representation of the diffraction pattern in (b) [1]. The presence of extra symmetric spots in the experimental diffraction pattern is due to double diffraction.
Fig. 3.6) (a) The microstructure of the sample heated up to 400°C with heating rate of 10°C/min. The EDS analysis indicates that the precipitates are either (b) Si or (c) β.

Fig. 3.7) The variation of hardness versus time for AA6022 during aging at 175°C. The peak hardness was obtained after 8 hours aging and Figure 3.8a shows the morphology of the precipitates in the peak-aged sample. The precipitates are needle-
shaped and the faint symmetrical streaks in the diffraction pattern (Fig. 3.8d) suggest that the precipitates are $\beta''$. Similar to the precipitates in the alloy at peak 3b, close examination of the end-on precipitates reveals that the lath-shaped precipitates also exist (see Fig. 3.8b). The lath-shaped precipitates were also observed by dark field imaging such as the image shown in Fig. 3.8c. The presence of lath-shaped precipitates in peak-aged Al-Mg-Si alloys with low Cu content was also reported by Sagalowicz et al [13] and Cayron et al [14].

Fig. 3.8) (a) The microstructure of the sample aged 500min at 175°C. The majority of the precipitates are $\beta''$ and a few lath-shaped precipitates are marked in the magnified image (b). (c) The dark field image of the reflections marked in the $<100>$ Al zone axes TEM diffraction (d).

To find out at what stage the lath-shaped precipitates formed, samples in different stages of aging prior to the peak of hardness were investigated by TEM. Figure 3.9 shows the bright field, dark field and SAD pattern of the sample heated at 175°C for 300min. Figure 3.9a clearly resolves very fine needle-shaped precipitates that are homogenously distributed in the matrix, the faint streaks in the SAD pattern (Fig. 3.9b) suggest that the
precipitates are \( \beta'' \). Close examination of the end-on precipitates indicates that the cross section is more likely polyhedral which is closer to the monoclinic base-centered crystal structure of \( \beta'' \) (Fig. 3.9c). Multiple areas were examined and no lath-shaped precipitates were found.

Fig. 3.9) (a) The microstructure of the sample aged 300 min at 175°C. (b) The SAD pattern in the \( <100> \) direction of Al zone axes suggests that the precipitates are \( \beta'' \). (c) The dark field image of the reflections indicated in (b) confirms that no lath-shaped precipitates are present.

Figure 3.10a shows the microstructure of the sample in a slightly over-aged (~730 min) condition. The majority of the precipitates are still \( \beta'' \) (Fig. 3.10b), but one can find a few large rod-like precipitates as well as lath-shaped precipitates which display the precipitate characteristics of the metastable \( Q' \) phase. Dark field imaging (Fig. 3.10c) of the microstructure confirms that the elongated dimension of rod-like precipitates is about 100-200 nm which agrees well with the reported data for \( \beta' \) precipitates [12,15]. Thus,
based on the information from DSC and TEM observations on samples heated at 10°C/min and isothermally aged specimens, one may conclude that following the growth of the β” precipitates, the precipitates transform to lath-shaped/Q’ and rod-like β’ precipitates. Electron diffraction analysis on Q’ phase by Chakrabarti and Laughlin [8] indicated that the lattice spacing of this phase in the c axis perfectly matches along the <100> aluminum directions. In addition the repeat distance along the <150> directions of the aluminum matrix is 1.03nm which is the same as the reported lattice parameter of the Q’ phase [1,2,8]. This may explain the transformation of some of the β” precipitates to lath-shaped precipitates during growth. Therefore instead of the sequence of Clusters / GP zones → β” → β’ + lath - like precipitates → β + Si proposed by Miao and Laughlin [1,2], the following sequence for precipitation of metastable phases in AA6022 samples is proposed:

Clusters / GP zones → small precipitates → \[\beta'' \rightarrow \beta' \]
\[\beta'' \rightarrow \text{lath shaped precipitates} \rightarrow Q' \rightarrow \beta + \text{Si} \]

3.5 Conclusions

The precipitate sequence in aluminum alloy 6022 was investigated by means of DSC and TEM. It was found that at early stages of aging there are some unknown small precipitates which form prior to the formation of β” precipitates and these were not reported in the previously suggested precipitation sequence for this alloy. These small precipitates form in the range of the paint baking process (~30min at 175°C) of this alloy and should be considered for any further alloy modifications required to increase the formability of this alloy.
Fig. 3.10) (a) The microstructure of the sample aged for 730min at 175°C. According to the SAD pattern in the <100> direction of Al the majority of the precipitates are $\beta''$. (c) Dark field imaging of the reflections indicated in (b) revealed the presence of a few $\beta'$ rods.

Our investigations on the precipitates of the peak-aged samples reveal that $\beta''$ is the major precipitate component but lath-shaped precipitates are also present. Studies on DSC and isothermally aged samples suggest that some of the $\beta''$ needles transform during growth to lath-shaped precipitates which are likely one of the Q' precursors. Based on our studies the following precipitation sequence in AA6022 is proposed:

Clusters / GP zones $\rightarrow$ small precipitates $\rightarrow$ \[
\begin{align*}
\beta'' & \rightarrow \beta' \\
\beta'' & \rightarrow \text{Lath shaped precipitates} \\
\end{align*}
\] $\rightarrow \beta + \text{Si}$
3.6 References


Chapter 4

4. The Effect of Dislocations on Precipitates in AA6022

4.1 Introduction

In the previous chapter the precipitate types and their sequence in AA6022 were characterized. The objective of the present chapter is to investigate the effect of dislocations on the precipitation sequence in AA6022 and to compare these with the precipitation sequence that was characterized in the previous chapter. It is found that $\beta''$ precipitates are replaced by $\beta'$ and $Q'$ in the predeformed samples. The results show that at higher temperatures only $Q'$ precipitates are present in the microstructure of the predeformed samples. Also the measured activation energy for precipitate formation in the case of predeformed and undeformed samples was compared. The results show that dislocations facilitate precipitation by decreasing the activation energy.

4.2 Background

While the decomposition of the supersaturated solid solution of the undeformed Al-Mg-Si alloys has been studied extensively, relatively few reports document the decomposition kinetics from the deformed state [1-4]. It is reported that introduction of deformation as part of the heat treatment process can significantly influence the age hardening of 6xxx series alloys [1,4]. The effect of cold deformation on the precipitation and ageing behavior depends on the level of deformation. However most of the results show that the dislocations have significant effect on the formation of GP zones and the nucleation and growth of the intermediate phases are accelerated largely by cold rolling.
HRTEM studies of Matsuda et al. [5] showed that Type-C precipitates (similar to Q'/Q) are typical in a deformed excess Si alloy whereas in balanced Al-Mg-Si no Type-C precipitates were found.

The present chapter concentrates on the characterization of the effect of dislocations on the metastable precipitates in AA6022 and to compare these with those in the undeformed state. Moreover, the role of dislocations on the kinetics of the precipitation during the decomposition of super saturated solid solution was studied.

4.3 Experimental Plan

The as received AA6022 plates were cold rolled to the final thickness of 0.58mm. The sheets were solution treated in a batch type furnace at 530°C for 30 min and water quenched to room temperature. Deformation was subsequently performed by rolling to final thicknesses of 15% or 30% high reduction. Discs with diameters of 3 mm were punched from cold rolled sheets for differential scanning calorimetry (DSC) work.

The DSC experiments were performed with scanning rate of 10, 15 and 20°C/min. To determine to which precipitation reactions the peaks on the DSC correspond, TEM observations were made on samples heated in the differential scanning calorimeter with the same condition of the DSC experiments. After observation of each DSC peak, the samples were immediately cooled in liquid Nitrogen to preserve the microstructure. TEM specimens prepared by twin jet polishing in solution of 30% HNO3 and 70% Methanol at ~20°C. TEM investigations were carried out in a Philips TM420 microscope operating at 120KV. All SADs in this work were obtained in <100>Al zone axes. Due to the strong contrast of dislocations and precipitates, it was very difficult to
carefully analyze the precipitate structures (especially precipitate cross sections) in <100> zone axes of Aluminum. The bright field images were obtained by tilting the sample holder less than 2 degrees away from <100> aluminum zone axes. This resulted in poor contrast for the dislocations, making them difficult to discern in the bright field images.

Fig. 4.1) DSC traces of AA6022 (a) in the as quenched condition, (b) after 15% deformation and (c) after 30% deformation.

4.4 Results

Figure 4.1a presents the DSC curve obtained at a heating rate of 20°C/min for the AA6022 immediately after solutionizing and quenching in water. The detailed analyses
of the precipitation sequence in this alloy were studied in the previous chapter. The characterized precipitates are summarized in Table 4.1.

Table 4.1) Analysis of the DSC curve in Fig. 4.1a

<table>
<thead>
<tr>
<th>Peak</th>
<th>Temperature Range (°C)</th>
<th>Precipitate Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67-185</td>
<td>GP zones/Clustering</td>
</tr>
<tr>
<td>2</td>
<td>213-272</td>
<td>β”</td>
</tr>
<tr>
<td>3</td>
<td>277-326</td>
<td>β’+Q’</td>
</tr>
<tr>
<td>4</td>
<td>331-450</td>
<td>β+Si</td>
</tr>
<tr>
<td>5</td>
<td>459-539</td>
<td>Dissolution of precipitates</td>
</tr>
</tbody>
</table>

Results on the effect of 15% and 30% deformation on DSC traces are shown in Figures 4.1b and 4.1c. It can be seen that the heat of reaction (area under the curve) for peak 1 has decreased by increasing the amount of deformation. The microstructure of samples heated up to peaks 1, 1’ and 1” were investigated by TEM and no sign of ordered precipitates was found.
Fig. 4.2) (a) Bright field TEM micrograph, (b) the corresponding [001]Al diffraction pattern, the \((21\bar{3}1)_Q\) and \((0\bar{3}21)_\beta'\) spots are labeled in the diffraction pattern accordingly and (c) schematic representation of the diffraction of AA6022 deformed 30\% and heated at a rate of 20°C/min to just beyond DSC peak 2° shown in Fig. 1c.

Figure 4.2 shows the TEM micrograph of the sample after being deformed 30\% and heated up to the end of peak 2°. The SAD pattern and close examination of the end-on precipitates revealed that precipitates with lath morphology in addition to the rod-like \(\beta'\) are present in the microstructure. The lath shaped precipitates have an angle of less than 11° with respect to the nearest \(<001>_{AI}\) direction in the matrix, which agrees with the
Q' phase characteristics [9]. Similar precipitate morphologies were observed for the 5% and 15% predeformed samples. Therefore the appearance of peak 2' and 2'' is due to the formation of Q'+β'.

![Micrographs](image)

Fig. 4.3) Bright field TEM micrographs of AA6022 heated at a heating rate of 20°C/min to the end of DSC (a) peak 3, (b) peak 3' and (c) peak 3'' shown in Fig. 4.1. (d) is the diffraction pattern corresponding to (c).
Figures 4.3 show the TEM bright field image of the samples heated up to 350°C in the undeformed and predeformed conditions. The Q′ phases clearly have rectangular cross sections in the viewing plane and have long dimension along <100>_{Al} directions.

4.5 Discussion

The high resolution TEM and atomic probe field ion microscopy (APFIM) analyses of Dutta et al [6] and Edwards et al [7] show that the clustering of Mg, Si and Mg-Si atoms and GP zones occur at the early stage of precipitation in Al-Mg-Si alloys. Therefore peaks 1, 1’, and 1” are probably related to atomic clustering and GP zone formation which are difficult to resolve with conventional TEM analysis. The activation energy for the clustering and GP zone formation has been reported by Gupta [8], Jena [9], and Doan [10] to be 79kJ/mole. This value is very close to the required activation energy for vacancy migration. Considering that excess vacancies exist in the as-quenched condition, this reaction can be explained in terms of vacancy cluster formation. According to Figure 4.1, deformation prior to DSC analysis reduces the heat of reaction for clustering/GP zone formation. This can be explained in terms of the effect of dislocation structure on the clustering/GP zone formation. The dislocation cell structure may act as a vacancy sink and retard the formation and development of clustering/ GP zone formation. Therefore the molar heat for this reaction decreases by increasing the amount of deformation.

Comparing Fig 4.1a with b and c indicates that deformation after quenching causes a slight shift (~25°C) in the temperature of peak 2 to the lower temperatures (peaks 2’ and 2”). Quaino and Yannocopulos [11] have also reported the decrease in the
temperature of peak 2 in predeformed AA6111. The results of Miao et al [12] show that the hardening in alloy 6022 is mainly caused by precipitation of peak 2 or the \( \beta'' \) phase during artificial aging at 175°C. Therefore peak 2 was studied with more detail and the kinetic data for the precipitation reactions associated with this peak in the deformed and undeformed conditions was measured. The DSC analyses were performed by using the method developed by Gupta, Lloyd and Jena [8-9,13-15]. Their analysis shows that the precipitation process in aluminum alloys is diffusion controlled and the temperature dependence of the precipitation rate \( \frac{dY}{dt} \) can be represented by an Arrhenius type equation in the following form:

\[
\frac{dY}{dt} = f(Y)k_0 \exp\left(\frac{-Q^*}{RT}\right)
\]

(4.1)

where \( k_0 \) is the frequency factor, \( Q^* \) is the activation energy, \( R \) is the gas constant, \( T \) is the absolute temperature and \( f(Y) \) is only dependent on \( Y \). Figure 4.4 shows that peak 2 precipitates shift to higher temperatures with increasing heating rate. This suggests that the process associated with the peak is temperature dependent. Therefore following Gupta and Lloyd [8], Jena et al [9], and Gupta et al [14], it is assumed that equation (4.1) can be used to calculate the kinetic data for peak 2 precipitates.
Fig. 4.4) β′ precipitation peaks in the as quenched alloy at 10°C/min, 15°C/min and 20°C/min heating rates.

Undeformed condition. The mole fraction of precipitates under peak 2, \( Y_2 \), can be expressed as:

\[
Y_2 = \frac{A(T)}{A(T_f)}
\]

(4.2)

where \( A(T) \) and \( A(T_f) \) are the increment area and the total area under the DSC peak 2 respectively. Using the chain rule, \( \frac{dY_2}{dt} = \frac{dY_2}{dT} \cdot \frac{dT}{dt} = \frac{dY_2}{dT} \cdot \phi \) and setting \( \phi = \frac{dT}{dt} \), the equation (4.1) can be re-written as,
\[ \frac{dY}{dT} \phi = f(Y)k_0 \exp\left(\frac{-Q^*}{RT}\right) \]  \hspace{1cm} (4.3)

Fig. 4.5) Plot after using equation (4) for calculating \( Q^* \) and \( k_0 \) based on assuming \( f(Y) = 1-Y \) for \( \beta' \) precipitation.

By assuming \( f(Y_2) = (1-Y_2) \) which agrees well with experimental data on aluminum alloys [8,9], the activation energy for \( \beta' \) precipitation can be derived from equation (4.3) as follows:

\[ \ln \left[ \frac{dY_2}{dT} \cdot \frac{\phi}{1-Y_2} \right] = \ln(k_0) - \frac{Q^*}{RT} \]  \hspace{1cm} (4.4)

The results for the heating rate of 20°C/min are plotted in Figure 4.5 over the range of values of \( Y \) from 0.1 to 0.9. The estimated average values for \( Q^* \) and \( k_0 \) are 260.6
KJ/mole and 4.2X10^{24} \text{ s}^{-1} \text{ respectively (Table 4.2). Therefore the formation of } \beta' \text{ precipitates can be characterized by the equation}

\[
\frac{dY_z}{dT} = (1 - Y_z) \times 4.2 \times 10^{24} \times \exp\left(-\frac{260.6K}{RT}\right)
\]

(Table 4.2) Measured activation energy and k0 values for peaks 2, 2' and 2'' precipitation

<table>
<thead>
<tr>
<th></th>
<th>As Quenched (peak 2)</th>
<th>Quenched and 15% Deformed (peak 2')</th>
<th>Quenched and 30% Deformed (peak 2'')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy, (Q^*) (kJ/mole)</td>
<td>260.6</td>
<td>138.4</td>
<td>104.2</td>
</tr>
<tr>
<td>(k_\theta) (s^{-1})</td>
<td>4.2 \times 10^{24}</td>
<td>2 \times 10^{12}</td>
<td>5.0 \times 10^{8}</td>
</tr>
</tbody>
</table>

It should be mentioned that the measured activation using this approach may not be an accurate estimation of barrier height to the precipitation of \(\beta''\). As a result of competing effects of volume free energy, atomic diffusion and interphase boundary energy during the formation of \(\beta''\), the barrier height can be temperature dependent. A more accurate calculation of activation energy requires a large amount of data on chemical interdiffusion in this Al-Mg-Si alloy and its transition phases and interphase boundary energies which is beyond the scope of the present work.

**Deformed condition.** Figure 4.6 shows the effect of predeformation on the precipitates of peak 2′ and 2''. As can be seen, deformation prior to heating the as quenched material shifted the peak temperature of peak 2 precipitates from 261°C to 241°C after 30% deformation (peak 2''). Similar to the above analyses the kinetic data for precipitates of
peaks 2` and 2” were calculated and the Q* and k₀ values are presented in Table 4.2. Our measured activation energy for 30% deformation agrees well with reported results of Long et al [1] which calculated the activation energy as 119KJ/mole.

According to work of Buinov [16], the plastic deformation had no significant effect on the decomposition rate of Al-1.4%Mg₂Si alloy. Long et al [1] demonstrated that the activation energy for the reaction 2 in Al-0.98%Mg-0.58 wt %Si alloy is not affected appreciably by cold rolling. However they have reported that cold rolling accelerates the aging process due to increase in pre-exponential factor and entropy of reaction. Our results show some differences from the work of Buinov and Long. As can be inferred from Figure 4.6, the introduction of dislocations has accelerated the formation of the precipitates of peak 2` and 2” in comparison to peak 2 precipitates and Table 4.2 shows that by increasing the amount of deformation the activation energy for precipitates of peak 2` and 2” decreases. This agrees well with results of Hirata and Matsue [17] who reported a decrease in the activation energy for the metastable phases in Al-Mg-Si alloys.
Fig. 4.6) $Y_2(T)$ versus temperature for (a) peak 2 precipitation, (b) peak 2’ precipitation (c) peak 2’’ precipitation.

The reason for reduction in activation energy can be explained by the effect of non-equilibrium defects such as dislocations produced due to deformation. Dislocations act as short-circuit paths for solutes and facilitate the atomic migration which in turn decreases the activation energy for the growth of precipitates. In addition, the solute atmosphere around dislocations enhances the rate of precipitation via an increase in the local chemical driving force [18].

By deforming the as quenched material, the pre-exponential factor has been decreased considerably (Table 4.2). This is related to the frequency factor of solute atoms for obtaining the activation energy to join precipitate nuclei during its growth. This can be explained by the fact that in the presence of dislocations, micro-segregation of the solute atoms at dislocation cells will occur [18], which in turn decreases the number of solute atoms available to take part in precipitate formation. According to equation (4.3), by decreasing the frequency factor the rate of precipitate formation should decrease.
However the decrease in activation energy dominates the effect of the pre-exponential factor on the precipitation rate and thus the total effect would be in the direction of increasing the precipitates of peak 2’ and 2” in comparison to peak 2 precipitates (Fig. 4.6).

Figure 4.2 shows the TEM micrographs of a sample heated up to 280°C (peak 2’ and 2’’) after being deformed 30%. Based on the diffraction patterns (Figs. 4.2b and c) and close examination of end-on precipitates (Fig. 4.2a), two types of the precipitates can be revealed in the microstructure, lath shaped Q’ and rod-like β’. Therefore the appearance of peak 2’ and 2’’ is due to the formation of Q’+β’. This results in higher overall reduction in the free energy formation of these two phases. Appearing single peak for the precipitation of Q’ and β’ suggests that both phases are likely to form simultaneously. This means that the calculated activation energy for peaks 2’ and 2” can be assumed to be the same for Q’ and β’.

The reason for the precipitation of Q’ and β’ instead of β” can be explained in terms of heterogeneous nucleation of precipitation due to the presence of dislocations generated by the cold-compression operations. Dislocations are favorable energy sites for precipitates [19] and short circuit path for solutes [20]. This promotes the precipitation of stable rather than metastable phases. This is in agreement with the previously reported results on the effect of dislocations on the precipitation process in 7xxx series aluminum alloys [20,21]. For example, Allen and Vander Sande [21] indicate that precipitation on dislocations appears directly as the equilibrium phase η instead of the metastable η’ phase.
In predeformed conditions, peaks 3’ and 3” are shifted to the higher temperatures (Fig 4.1b and c). This behavior may be explained by recrystallization phenomena. The work of Long and Ohmori [1] on Al-Mg-Si alloys show that after 20% deformation recrystallization occurs above 300°C. Therefore the softening process in the deformed specimens may be a reason for the retardation of peak 3. It can be seen from Fig. 4.3 that, while in the undeformed sample (Fig. 4.3a) both rod like β’ and lath like Q’ precipitates are present in the precipitation reactions correspond to peak 3, in predeformed samples (Figs. 4.3b and c) only lath shaped precipitates, Q’, are seen in peaks 3’ and 3”. Therefore, one can conclude that the presence of dislocations promotes the formation of the Q’ phase. Similar observations have been reported by Deschamps et al [22] and Ringer et al [23]. Ringer et al [23] showed that despite similarities in the morphology and crystallography of Ω and T₁ phases, cold-working prior to aging promoted the precipitation of T₁ in an Al-Cu-Li-Mg-Ag alloy and decreased the density of Ω phases in an Al-Cu-Mg-Ag alloy. According to Figs. 4.1b and c, there is no endothermic reaction between peaks 2’ and 3’, or peaks 2” and 3” which indicates that the β’ precipitates were not dissolved, but more likely transformed to Q’. It should be noted that both β’ and Q’ phases have hexagonal crystal structure, and such a transformation may not be predictable. However, it can be explained by the fact that the habit plane of Q’ has been determined to be {150} of the aluminum matrix [24]. The repeat distance along the <150> directions of the aluminum matrix is 1.03 nm which is about the same as the lattice parameter of the Q’ phase [25]. Therefore the precipitates tend to form as a lath so as to minimize the misfit in its surface and hence its energy. This may also explain the lower heat of reaction for peak 3’ and 3” in the deformed condition in comparison to the
undeformed sample. While in the undeformed condition peak 3 is due to the formation of both \(\beta'\) and \(Q'\) precipitates, peaks 3' and 3'' in the deformed condition are only due to the transformation of \(\beta'\) to \(Q'\). Therefore instead of the sequence

\[
\text{Clusters / GP zones} \rightarrow \beta'' \rightarrow \beta' + Q'
\]

for the metastable phases in the undeformed condition, the following sequence for precipitation of metastable phases in the dynamic heating scenario of a DSC scan at 20°C/min of predeformed AA6022 samples is proposed:

\[
\text{Clusters / GP zones} \rightarrow \beta' + Q' \rightarrow Q'
\]

### 4.6 Conclusions

The effect of predeformation on the precipitation reactions of an Al-Mg-Si alloy (AA6022) was studied by DSC and TEM. Thermograms of samples at different levels of deformation were used to calculate the kinetic data of precipitation reaction rate. It was found that deformation of as-quenched samples decreased the activation energy for peak 2' and 2'' precipitates and the pre-exponential factor, \(k_0\). However, the effect of activation energy dominates and the precipitation reaction in peaks 2' and 2'' are accelerated in comparison to peak 2 precipitates.

It was found that while the second exothermic peak (peak 2) in the undeformed sample is due to \(\beta''\) precipitates, the second exothermic peaks (2' and 2'') in the predeformed samples are due to \(\beta' + Q'\) precipitates. Our investigations on peak 3 precipitates of the undeformed sample show that the precipitates are \(\beta' + Q'\). Corresponding peaks 3' and 3'' in the predeformed samples are due only to \(Q'\). It was concluded that the \(Q'\) precipitates are more likely to form by heterogeneous nucleation processes. Therefore, instead of the sequence

\[
\text{Clusters / GP zones} \rightarrow \beta'' \rightarrow \beta' + Q'
\]
metastable phases in the undeformed condition, the following sequence for precipitation of metastable phases in the dynamic heating scenario of a DSC scan at 20°C/min of predeformed samples is proposed:

\[ \text{Clusters} / \text{GP zones} \rightarrow \beta' + Q' \rightarrow Q' \]
4.7 References


5. Characterization of Dislocation Structures and Orientation Evolution in the Presence of Precipitates

5.1. Introduction

Dislocation structure and orientation evolution during deformation of aluminum alloys was investigated experimentally using channel die compression followed by electron backscatter diffraction (EBSD) and TEM. Polycrystalline AA6022 samples were aged and then deformed up to 10% and 20% strain. Local misorientation associated geometrically necessary dislocation content was studied for large grains with <110> orientations as a function of precipitate characteristics. It is found that precipitate morphology affects the density and distribution of geometrically necessary dislocations. Also, a significant orientation spreading was observed for the specimens at the peak-aged condition while it was less considerable for the overaged condition.

5.2. Background

Non-uniform plastic deformations give rise to the development of the so-called geometrically necessary dislocation (GND) densities which are required to accommodate lattice curvature [1]. Although the concept of geometrically necessary dislocations (GNDs) has been a subject of extensive discussion in the literature (e.g., [1] and [2]), the formation and evolution mechanisms of the GND cell structures are not well established. Also, it is well known that precipitates reduce anisotropy and affect the texture evolution in the given material (e.g. [3]). However a systematic study on the behavior of GND and
local orientation evolutions in the presence of precipitates is missing in the literature. In a previous study [4], the effect of crystal lattice orientation and the orientations and topology of neighboring grains on the evolution of dislocations was investigated. In this chapter, the evolution of GNDs and orientation evolution in the presence of different precipitate morphologies is investigated.

5.3. Experimental Plan

To produce precipitates with different morphologies, aluminum alloy 6022 (Al-0.55%Mg-1.1%wt Si) was solutionized for 3 hours at 550°C and subsequently quenched in water. The specimens were aged at 175°C in a salt bath furnace and the precipitates were characterized by TEM prior to deformation. EBSD analysis on the aged samples showed that very large grains (~2mm diameter) with orientation of <110> are present in the microstructure. These large grains are ideal for use in studying GND evolution since they are surrounded by much smaller grains which form an essentially homogenous medium. Each large grain has the same orientation and is embedded in a homogeneous matrix so they can be reasonably compared with one another. After ageing, channel die compression experiments were performed up to the level of 20% deformation. Subsequently orientation measurements were obtained by EBSD at a 3 micron step size from large grains near the central region of the channel die deformed specimens. The other existing orientations in the EBSD scan were excluded from the data.
5.4 Results and Discussion

Fig. 5.1 shows the bright field TEM micrograph of specimens aged for 500min and 5500min. The ageing kinetics and precipitation sequence of this alloy has been investigated by the authors and discussed in Chapter 3. The results show that the precipitates in Fig. 5.1a and b are $\beta''$ and $\beta' + Q'$ respectively. The $\beta''$ precipitates are needle shaped and are aligned in the $<100>_{\text{Al}}$ direction of matrix (Fig. 5.1a). The longer dimension of needles is in the range of 20 to 40nm which agrees well with those reported in literature. In contrast, the $\beta' + Q'$ precipitates are widely spaced and are much larger than the $\beta''$ precipitates (Fig. 5.1b).

The GND density can be obtained according to Nye [5] equation which relates the second-rank curvature tensor, $\kappa_{ij}$, directly to the dislocation density tensor, $\alpha_{ij}$:

$$\alpha_{ij} = \kappa_{ij} - \delta_{ij} \kappa_{kk}$$  \hspace{1cm} (5.1)
where $\delta_{ij}$ is the Kronecker delta and the summation convention is adopted. According to the recent work of El-Dasher et al [6,7] the curvature tensor can be measured by the automated EBSD technique and for FCC materials the density of geometrically necessary dislocations can be obtained by,

$$
\rho_{GN} = A^T (AA^T)^{-1} \alpha
$$

(5.2)

where the matrix $A$ represents a component of the dislocation dyadic. Based on this method the total GND density for the large grains with $<110>$ orientations in two different samples with different precipitate morphologies were calculated and the GND distribution in the grains were plotted in Fig. 5.2a and b. The total GND density in the sample aged up to the peak of hardness ($\sim$500min) is 25% higher than the overaged ($\sim$5500min) sample. The reason can be explained by the fact that the needle shaped precipitates are the strongest barrier to the motion of dislocations and therefore more dislocations are expected to pile up around these precipitates. Thus the lattice rotation associated with these precipitates would be higher. In contrast, the overaged precipitates are large and the space between them is wide, therefore the dislocations can overcome them more easily and the lattice rotation would be less for this type of structure. From these results one can conclude that the precipitate morphology strongly affects dislocation flow and patterning, which yields a change in the GND densities and their distribution.
Fig. 5.2) GND distribution plot for the samples aged (a) 500min (b) 5500min and then deformed 10% (c) GND density comparison for these two samples after 0 and 10% deformation.

The local orientation evolution within individual grains was studied during deformation up to 5%, 10% and 20%. There was no significant orientation evolution in the samples deformed up to 5% and 10%, and thus are not discussed here. Figure 5.3 shows the orientation evolution during deformation up to 20% in the overaged specimens. As can be seen from pole figures and <001> IPF maps, the initial orientations within the grains (Fig. 5.3a) and orientations after 20% (Fig. 5.3b) are almost similar and are close to <110>.
Fig. 5.3) The orientation evolution in the overaged specimens; (a) after 0% deformation, and (b) after 20% deformation.
Fig. 5.4) The orientation evolution in peak-aged specimens; (a) after 0% deformation (b) after 20% deformation.

Figure 5.4 shows the orientation evolution during deformation up to 20% in peak-aged specimens. One can see that although the initial orientations within a grain (Fig. 5.3a) are close to <110>, the orientations spread after 20% deformation (Fig. 5.3b). This can be inferred by comparing the (101) and (111) pole figures and <001> IPF maps. Also comparing the color scales indicates that the degree of randomization in the peak-aged
samples is increased 10 times where this is 4 times for the overaged samples. The similar explanation given for local GND evolution can be used to justify the orientation evolution behavior of peak-aged and overaged samples. In the peak-aged condition, the pile up of dislocations around the semi-coherent needle-shaped $\beta''$ precipitates results in significant local lattice rotations which in turn increase the orientation spreading within individual grains. However, the overaged precipitates, $\beta'$ and $Q'$, are large and the space between them is wide, therefore dislocations can overcome them more easily and the lattice rotation and thus orientation spreading would be less for this type of structure. From these results one can conclude that the precipitate morphology strongly affects dislocation and orientation evolution within individual grains.

5.5 Conclusions

This study demonstrates a clear dependency of GND and orientation distribution within the individual grains on the character of precipitates. It is shown that the presence of the semi-coherent $\beta''$ precipitates associated with the peak-aged condition resulted in significant increase in GND density and local misorientation within the grains. However these effects were insignificant for the $\beta'$ and $Q'$ associated with the overaged condition.
5.6 References


6. Microstructure Evolution and Observed Stress Response during Hot Deformation of 5005 & 6022 Al Alloys

6.1 Introduction

The mechanical response of material is strongly dependent on the details of the starting microstructure. The objective of this chapter is to experimentally and statistically analyze the effect of physically measurable features of the starting microstructure on the yield stress of 6022 Al alloy. In this study, two commercially used AA5005 and AA6022 Al alloys were deformed at various combinations of processing parameters (such as strain, strain rate and temperature) to produce samples with a variety of microstructures. Quantitative parameters obtained from microstructural characterization and stress analysis were performed by a multiple regression analysis technique to determine the relative influence of various microstructural parameters on the observed stress response. The geometrically necessary dislocation (GND) density was determined to be the most important measured parameter affecting the yield stress. Experimental and statistical analysis showed a linear relationship between yield stress and square root of GND density. A statistical formulation was used to develop the yield strength model for 6022 Al alloy as a function of microstructural parameters.

6.2 Background

A proper understanding of the relationships that connect processing conditions, microstructural evolution and mechanical properties is important for any materials
scientist to improve productivity and product quality. Optimization of fabrication processes requires a profound understanding of the microstructure evolution at various length scales. There are many different scenarios in which microstructural prediction is particularly valuable such as:

a. where microstructure is critical in controlling final properties (e.g. toughness of steel welds) or subsequent material processability (e.g. earing in drawing of sheet metal);

b. where process optimization requires knowledge of microstructural limits (e.g., maximum welding or extrusion speeds);

c. where microstructure captures the coupling through multi-stage processes, giving opportunities for alloy and process development (e.g., effect of homogenization on precipitation after extrusion, or the effect of prior forming and heat treatment on weldability).

Many aspects of microstructure modeling and microstructure-property relationships have been studied, however the understanding is still incomplete especially in the area of size dependent material behavior. There are many experimental observations which indicate that, under certain specific conditions, the specimen size may significantly affect deformation and failure of the engineering materials and a length scale is required for their interpretation. Experimental observations indicate that material hardening increases as the size of material decreases. This dependence of mechanical response on size could not be explained by the classical continuum mechanics since no length scale enters the constitutive description. However, gradient plasticity theory has been successful in
addressing the size effect problem. Thus GNDs has received lot of attention recently, however no specific attempt has been made to relate the experimentally measured GNDs to the stress response.

The present study is an effort to incorporate experimentally determined density of geometrically necessary dislocations (GNDs) into a statistically formulated model of deformation response. GNDs are defined as dislocations needed to accommodate the difference in crystal lattice rotation produced by different slip system activity from point to point within a given grain [1-4]. It is possible to get an estimate of GND density from spatially specific orientation measurements such as those obtained from automated EBSD analysis. Some other microstructural parameters that describe misorientation within a grain are grain orientation spread (GOS) and grain average misorientation (GAM). GOS is a measure giving the algebraic average of the misorientation angle between all points (whether adjacent or otherwise) within a given grain. GAM is a second measure that gives the algebraic average of the misorientation between all points and their nearest neighbor measurement points. Even though all of the above 3 microstructural parameters (GND density, GOS and GAM) provides a scalar number that describes the misorientation within a grain, computation of GND density provides additional information about the spatial distribution of densities of individual dislocation types that are required to support lattice curvature during deformation. Orientation spread within a grain arises, when stressed, because of differential rotation of crystallite regions (both in terms of angle and direction) within a grain. Development of in-grain orientation spread affects the mean free path of dislocation and therefore alters the stress required for
deformation. Other microstructural features measured were grain size, inter-particle spacing, volume fraction of precipitates, and radius of precipitates.

Following are the major areas of investigation in the following discussion:

i. Investigate the effect of GND and other microstructural parameters on the observed stress response.

ii. Compare the experimentally observed microstructural evolution during annealing and deformation of 5005 and 6022 Al alloys.

iii. Develop a model based on statistical formulation that predicts the yield stress of 6022 alloy as a function of experimentally measured microstructural parameters.

6.3 Experimental Plan

Flat samples with dimensions of (25 x 10 x 4) mm$^3$ were cut from hot rolled plates of 5005 and 6022 Al alloys and annealed at 520°C for 30 mins. Three samples (to form each batch for hot deformation) were placed on top of one another and deformed using channel die compression such that the direction of material flow is parallel to the direction of rolling (Figure 6.1). Various combinations of processing parameters (i.e. temperature of 250°C, 350°C and 450°C, strain of 10%, 20% and 30%, and strain rate of 0.01, 0.1, 1 s$^{-1}$) were applied during hot deformation to generate a variety of microstructures. Table 6.1 shows the deformation conditions used for 5005 and 6022 alloys. Microstructural analysis of the hot deformed samples was done along the long transverse cross-section using a scanning electron microscope equipped with EBSD. Texture analysis was performed using EBSD scans with a step size of 10 μm and the dislocation structure analysis was done using a step size of 0.2 μm. Backscatter electron
imaging, which provides compositional contrast, was used to detect precipitates in AA6022. Image analysis software was used to characterize precipitates in AA6022 in terms of inter-particle spacing, area fraction and radius of precipitates. Three miniature sized dog-bone

![Fig. 6.1) Schematic showing the process of channel die deformation used in this study.](image)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Strain</th>
<th>Strain Rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>25%</td>
<td>0.01</td>
</tr>
<tr>
<td>450</td>
<td>38%</td>
<td>0.01</td>
</tr>
<tr>
<td>450</td>
<td>40%</td>
<td>0.1</td>
</tr>
<tr>
<td>450</td>
<td>24%</td>
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</tr>
<tr>
<td>450</td>
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<td>1</td>
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<td>350</td>
<td>11%</td>
<td>1</td>
</tr>
</tbody>
</table>
samples (gage length – 10 mm and thickness – 2mm) were prepared from each batch of hot deformed samples and room temperature tensile testing was performed to failure with a constant crosshead speed of 0.005 in/sec. Statistical regression analysis was performed using MINITAB-14.0 (a commercial statistical and graphical analysis software package from Minitab Inc.) with an input of parameters from microstructural characterization and stress analysis.

6.4 Results and Discussion

The major focus of this chapter is to quantitatively understand the influence of experimentally determined GND density on the observed stress response during deformation. We chose two commercially used Al alloys 5005 and 6022 for this study with a chemical composition shown in Table 2.1. It is known that in AA5005, Mg forms a substitutional solid solution with Al, whereas in AA6022 precipitates of Mg$_2$Si form in an Al matrix. In the following part of the chapter, the first three sections are devoted to the comparison of experimentally observed microstructural evolution and stress-strain behavior of 5005 and 6022 alloys and the last two sections are devoted to the development of a yield strength model for 6022 alloy. The GND density is determined to be the major microstructural parameter, sufficient enough to represent all characteristics of dislocation structures, affecting the yield strength.

6.4.1 Characterization of Starting Material

Figure 6.2 contains boundary images of hot rolled 5005 and 6022 alloys obtained from EBSD; each line in both images represent misorientation of 1º or higher. Dense
dislocation cell structure is observed in all the grains, irrespective of their crystal lattice orientation. The density of dislocation cell structure appears to be same for both the alloys. It can be seen from Figure 6.2 that no recrystallization occurred during hot deformation, since all the grains possessed dislocation cell structure. The number fraction of grain boundaries with misorientation of 1-5° was approximately 48-57%; 5-10° was 25-27%; and 10° and higher was 18-24% for both the alloys. This indicates that significant number of dislocation cells contained high angle grain boundaries with misorientation greater than 5°. Higher misorientation across the cell boundaries occurs during hot deformation primarily by recovery processes that increase the dislocation content at the boundaries. Most of the grains possessed an aspect ratio of 0.63 for both alloys indicating preferential elongation in the direction of rolling, which is expected during deformation. The average grain sizes measured in the plan section of the samples were 38 µm and 35 µm for 5005 and 6022 alloys respectively. The average grain orientation spreads were 3.97 for 5005 alloy and 2.95 for 6022 alloy and the grain average misorientations were 2.37 for 5005 alloy and 1.97 for 6022 alloy.

Both alloys were annealed at 520°C for 30 mins to recrystallize the microstructure and reduce the total dislocation content. Figure 6.3 shows orientation images of 5005 and 6022 Al alloys after recrystallization. It can be seen that all the grains are almost free from dislocation substructure.
Fig. 6.2) Boundary maps showing well recovered microstructure after hot deformation for (a) 5005 and (b) 6022 Al alloys. Each line in the images represent misorientation of 1° or higher.

The average grain orientation spread reduced to 0.91 and grain average misorientation reduced to 0.84 after annealing. During recrystallization small, strain free grains are nucleated and grow in the deformed matrix. As these grains grow and consume the matrix, the dislocations in the matrix are absorbed and essentially get annihilated at the boundaries of the newly formed grains. When the new grains impinge upon one another, the process of recrystallization is complete. The kinetics of recrystallization are very dependent on a large number of external variables, the most important of which are probably the amount of pre-strain, the purity of the material and the orientation difference between recrystallized grain and the matrix into which it is growing. An inhomogeneous grain size observed in 5005 alloy is believed to be due to extra annealing of the material above recrystallization treatment leading to a grain growth of few grains.
Fig. 6.3) Orientation images of (a) 5005 and (b) 6002 Al alloys after recrystallization treatment. The orientation shading key is shown at the right.

6.4.2 Effect of Processing Parameters

Industrial processing of metals and alloys requires application of a wide range of processing parameters such as strain, strain rate and temperature, which influence the microstructure evolution and the kinetics of deformation. Various approaches have been used in the past in the area of microstructural modeling with the length scales ranging from atomistic, to slip system activity, to grain structure and continuum level. It is important to have statistically reliable and experimentally verifiable information about the microstructural evolution and stress response as a function of processing parameters to validate such models. Such understanding is important to define mechanisms driving microstructural evolution during thermo-mechanical processing and can be applied to develop processes that produce materials with a microstructure just good enough for a
desired application. This section discusses the effect of processing parameters on the stress response and texture evolution of both alloys.

Figure 6.4 contains a plot of the Zener-Holloman parameter (temperature modified strain rate \( Z = \dot{\varepsilon} \exp \left( \frac{U}{RT} \right) \)) versus flow stress obtained during channel die deformation for both alloys [5]. In the above equation \( \dot{\varepsilon} \) is applied strain rate, \( R \) is the gas constant, \( T \) is the absolute temperature and the activation energies, \( U \) (obtained from commonly selected values for Al alloys) used for the calculation were 156 kJ/mole and 140 kJ/mole for 6022 and 5005 Al alloys respectively. In accordance with earlier experimental observations and theoretical understanding, it can be seen from Figure 6.3, that higher flow stress is observed for samples deformed at high \( Z \) (i.e. low \( T \) and high \( \dot{\varepsilon} \)). Also the plot describes the effect of alloy chemistry on the deformation behavior of the two alloys at high temperatures. Trivedi et al. [6] studied the room temperature small strain (up to 10%) deformation behavior of AA5005 and AA6022 and observed that AA6022 generated a higher increase in dislocation structure (and correspondingly flow stress) with strain than AA5005. However a reverse effect is observed from Figure 6.3 during hot deformation in the sense that, at low values of \( Z \) (i.e. at low \( \dot{\varepsilon} \) and/or high \( T \) AA5005 showed higher flow stress than AA6022. This suggests that under the current experimental conditions, solid solution hardening observed in AA5005, is more effective in resisting deformation, especially for samples deformed at low \( Z \) values (i.e. at high \( T \).
Fig. 6.4) Plot showing flow stress obtained during channel die compression as a function of $Z$ for both 5005 and 6022 Al alloys.

and low $\dot{\varepsilon}$), than precipitation hardening in AA6022. The difference in stress-strain behavior during channel die compression between the two alloys can be due to the difference in starting microstructure and/or their alloy content. Since both alloys were fully annealed before hot deformation, AA6022 has a distribution of coarse overaged particles, which are easily bypassed by dislocations and hence do not significantly, contribute to strengthening. Solute atoms in AA5005 are in solid solution even during high temperature deformation and therefore possess higher ability of resisting deformation at higher temperatures.
Figure 6.5 contains the (001) pole figures showing predominantly cube texture of AA6022 after hot deformation at various processing parameters. In contrast AA5005 showed (Fig. 6.6) an ND rotated cube texture under similar deformation conditions due to the presence of large grains having a rotated cube orientation in all the samples. Since both the alloys were subjected to similar deformation conditions, the difference in texture evolution is due to the difference in alloy content of the two alloys.

6.4.3 Effect of Microstructure

This section is devoted to the influence of starting microstructure (specifically density of GND) on the different stress responses observed during tensile testing.

Texture evolution after channel die deformation was similar under all deformation conditions for both alloys – predominantly cube for 6022 alloy and predominantly rotated cube for 5005 alloy. Therefore the effect of texture on stress response during subsequent tensile deformation was neglected. Figure 6.7 shows a plot of change in the flow stress for both alloys as a function of deformation conditions. Change in flow stress was calculated as percentage difference in stress (at a particular value of strain) obtained after room temperature tensile deformation compared to stress obtained after high temperature channel die deformation. A relatively higher increase in flow stress was observed in AA6022 especially for samples previously deformed at low $Z$ values. This is because samples deformed at low $Z$ showed relatively higher density of GNDs in the final microstructure and therefore contributed to higher flow stress during subsequent tensile deformation.
Fig. 6.5) (001) texture pole figures of 6022 Al alloy showing predominantly cube texture for samples deformed under various processing conditions.

Figure 6.8 shows the variation in the 0.2% yield stress, obtained during room temperature tensile testing, with square root of GND density for 6022 alloy. Details about the calculation of GND density is described in Chapter 5. It can be seen that with increasing GND density the stress required for plastic deformation for both alloys increases. Such a
Fig. 6.6) (001) texture pole figures in 5005 Al alloy showing predominantly rotated cube texture for samples deformed under various processing conditions.

direct relationship between dislocation density and flow stress has been suggested by various modelers [7] with an equation of the type

$$\sigma = \sigma_0 + \alpha GbM \sqrt{\rho_f}$$

(6.1)
where $\sigma$ is the macroscopic stress response, $\sigma_0$ is the friction stress, $M$ is the Taylor Factor, $G$ is the shear modulus, $\alpha$ is constant and $\rho_f$ is the density of forest dislocations.

![Plot showing variation in % change in flow stress versus deformation conditions (described by Z * strain) for 5005 and 6022 Al alloys.](image)

Forest dislocations in the above equation include both GNDs and statistically stored dislocations (SSDs), formed by statistical mutual trapping of dislocations such as dislocation dipoles. In the current analysis we have ignored the effect of statistically stored dislocations on the stress response because of difficulties associated with determining the content of SSDs. It is known that at high temperatures Al alloys tend to form well-organized cell structures separated by dislocation cell walls creating small misorientations across them. Dislocations along those cell walls develop lattice curvature and contribute to GNDs. In the current experimental conditions most of the microstructure consists of those cell walls (and consequently the microstructure should be
dominated by GNDs) and therefore it may be reasonable to ignore the effect of SSDs on the stress response. In the present study it is assumed that SSDs and GNDs scale similarly, so measuring one or the other will yield the desired relationships. The effect of GNDs on the stress response is evident in Figure 6.9, which shows the stress-strain curves obtained during RT deformation for 6022 alloy plotted as a function of GND density.

![Graph showing variation in 0.2% yield stress (MPa) obtained during tensile testing with square root of GND density (x10^8/m) for 6022 Al alloy.](image)

Fig. 6.8) Plot showing variation in 0.2% yield stress (MPa) obtained during tensile testing with square root of GND density (x10^8/m) for 6022 Al alloy.

During the process of plastic deformation, dislocations have to overcome both short-range and long-range obstacles. For FCC metals, the primary short-range barriers are other dislocations which intersect the slip plane and impede the motion of gliding
Fig. 6.9) Stress-Strain curve of AA6022 for samples containing different GND densities in the starting microstructure.

dislocations. The evolution of SSDs during crystallographic slip increases the number of short-range interactions and accordingly results in isotropic hardening of the metal. Furthermore, the absolute GND densities equally well contribute to this short-range effect. The resistance to crystallographic slip due to short-range obstacles can be overcome by thermal activation, whereas effect of the long-range obstacles is essentially independent of the temperature, and can be overcome with the aid of the applied resolved shear stress. It is believed that the GNDs are responsible for the long-range contribution and they originate from any macroscopically inhomogeneous plastic deformation after removal of external loads.

Influence of GNDs on stress response was particularly studied by Hansen and Juul-Jensen [8] and they suggested that strengthening due to GND follows a Hall-Petch type equation:
\[ \sigma_{GBN} = K_1 \sqrt{G \cdot b / D_{GNB}} \]  

(6.2)

where \( K_1 \) is constant and \( D_{GNB} \) is the spacing between geometrically necessary boundaries (GNBs). Figure 6.10 is the TEM image showing geometrically necessary boundaries and incidental dislocation boundaries (IDB) in deformed Ni [9].

![Fig. 6.10) TEM image of deformed Ni showing geometrically necessary boundaries and incidental dislocation boundaries.](image)

TEM investigation showed that GNBs are produced by GNDs at medium to high strain and that they have preferred crystallographic orientation. With increasing strain, misorientation across GNBs increases and the spacing between them decreases due to accumulation of GNDs. It is also experimentally verified that these boundaries can have large misorientations across them (10-15\(^\circ\)) and are capable of restricting glide. Such observations clearly explain the effect of GND density on the stress response observed in the current analysis (Figures 6.8 and 6.9).
6.5 The Model

Many experimental studies on metals and alloys suggest that the macroscopic flow strength of the material is given by

\[ \sigma = \sigma_0 + \sigma_d \]  

(6.3)

where \( \sigma_0 \) is the friction stress and \( \sigma_d \) is the strength contribution due to dislocation structure. In the case of precipitation hardening systems (such as in AA6022 in the present analysis) or solid solution hardening systems (such as AA5005), there should be an additional term describing their effect in Equation 6.3. A linear addition of strength contribution due to the matrix, precipitates and solid solution has been suggested by various modelers [10-12]. Depending on the type of systems (precipitation hardening or solid solution hardening), the flow stress relationship then becomes

\[ \sigma = \sigma_0 + \sigma_d + \sigma_p (\sigma_{ss}) \]  

(6.4)

where \( \sigma_p \) and \( \sigma_{ss} \) are the strength contribution due to precipitates and solid solution respectively. It is known based on a large number of experimental data of metals and alloys that the strengthening due to dislocation structure is related to the dislocation density by the relation

\[ \sigma_d = \alpha(\dot{\varepsilon}, T)MGb\sqrt{\rho_T} \]  

(6.5)

where \( \alpha \) is a material parameter, \( G \) is the shear modulus, \( b \) is the Burger’s vector and \( \rho_T \) is the total dislocation density [7]. As mentioned earlier the total dislocations can be divided into two different categories: statistically stored dislocations (SSDs) and geometrically necessary dislocations (GNDs) and so Equation (6.5) becomes
Also, based on current experimental observations, SSDs and GNDs scale similarly and therefore assuming that the effects of SSDs and GNDs are proportional, we get

\[ \rho_{SSD} + \rho_{GND} = \rho_{GND}(p + 1) \]  

(6.7)

where \( p \) is a proportionality constant. Including \( \sqrt{(p+1)} \) in the material constant \( \alpha \), Equation (6.6) becomes

\[ \sigma_d = \alpha MGb \sqrt{\rho_{GND}} \]  

(6.8)

To describe the effect of precipitates (\( \sigma_p \)) we are considering the model proposed by Deschamps and Brechet [13] such that the strengthening due to particles follows the relationship

\[ \sigma_p = \frac{M \bar{F}}{bL} \]  

(6.9)

where \( \bar{F} \) is the mean obstacle strength and \( L \) is the average inter-particle spacing. The above equation assumes homogeneous distribution of particles such that dislocations have to pass through all the obstacles to cause deformation. Depending on the initial characteristics of the precipitates, \( \bar{F} \) and \( L \) will evolve with aging time and processing conditions. For coherent fine particles, the obstacle strength \( \bar{F} \) is dependent on particle radius and for coarse and overaged particles, obstacle strength \( \bar{F} \) is constant. Deschamps and Brechet further developed Equation (6.9) for the case of all precipitates being bypassed by the dislocations (which is the case in AA6022 in the current work) such that

\[ \sigma_p = \frac{kMGBf_v^{1/2}}{R} \]  

(6.10)
where $k$ is constant (usually 0.6-0.7), $G$ is the shear modulus, $f_v$ is the volume fraction of precipitate particles, and $\bar{R}$ is the mean radius of precipitates. Incorporating the effect of dislocation and precipitate structures into Equation (6.4), we get

$$\sigma = \sigma_0 + \alpha M G b \sqrt{\rho_{GND}} + \frac{k M G b f_v^{1/2}}{\bar{R}}$$

### 6.5.1. Regression Analysis

Microstructures of materials can be described by various structural parameters and each variable can potentially have a dominating effect on certain properties exhibited by the material. Therefore the selection of a microstructural variable of importance should depend on the desired property (response variable). One of the ways to extract the information about which microstructural features are dominant is by using statistical analysis. In the current chapter we use multiple regression analysis to investigate the effect of various experimentally measured microstructural parameters on the response variable. Regression analysis is a method that can be used to quantify the relationship between two or more predictor variables ($X$) and a response variable ($Y$) by fitting a line or plane through all the points such that the fitted line or plane minimizes the sum of the squared deviations of the points from the fitted values [14]. The response variable chosen was 0.2% yield strength determined from room temperature tensile testing.

Various microstructural parameters measured were grain size, grain orientation spread, grain average misorientation, density of geometrically necessary dislocations, and some of the precipitates characteristics such as average inter-particle spacing, area fraction of precipitates, and mean radius of precipitates. A similar parametric study in
single crystal Ni was performed by Horstemeyer [15] using the analysis of variance (ANOVA) technique with an input of data from MD simulation. He divided various parameters such as crystal orientation, strain rate, temperature, deformation path, x, y, and z dimensions into different levels in the analysis. In the current chapter processing parameters such as strain rate and temperature were not included in the analysis because stress parameters (forming response variable in the regression analysis) were obtained from room temperature and constant strain rate experiments. In the current regression analysis we included the actual values of quantitative parameters that describe different microstructural features rather than dividing them into various levels to allow more degrees of freedom (and obtain least error mean square).

6.5.2. Application to AA6022

When all the microstructural parameters such as grain size, density of GND, grain orientation spread, grain average misorientation, average inter-particle spacing, average particle radius and area fraction of precipitates were incorporated in the regression analysis, large ‘P’ values were obtained for all the parameters (Plot 6.11a). This indicates that such combinations of microstructural parameters fed into the analysis are ineffective in describing the stress response due to existing correlations between them. The matrix of correlation between various microstructural features was determined and it was observed that there exists a relatively strong correlation between density of GND and GOS, GOS and GAM, density of GND and inter-particle spacing. Various combinations of microstructural parameters were fed into the regression analysis to determine major parameters that influence yield strength. The regression equation that best defines the
relation and the one that gave minimum ‘P’ values for corresponding microstructural parameters was

$$\sigma_y (MPa) = -111 + 0.000001 \sqrt{\rho_{GND}} (m^{-1}) + 0.000045 \sqrt{f_v R} (m^{-1})$$  \hspace{1cm} (6.12)

It is interesting to note that the regression equation obtained for the yield stress (Equation 6.12), by choosing the parameters that give minimum ‘P’ values, is similar to the one proposed by Deschamps et al. in Equation (6.11). ‘P’ values obtained during the regression analysis (Plot 6.11b) suggest that the GND density explains more variation in the yield strength than the characteristics of particles.

Fig 6.11) Summary of regression analysis showing influence of microstructural parameters on the yield stress of 6022 Al alloy.

This in fact is believable and precipitates do not significantly affect the yield stress because precipitates in AA6022 are overaged and so dislocations can bypass them easily. The strength contribution due to precipitates is directly related with volume fraction of precipitates suggesting that with increase in volume fraction of precipitates in
the matrix, the number of obstacles to dislocation motion also increases, which eventually increases the stress required for plastic deformation. In the current analysis the strength contribution due to dislocation structures is considered to be only due to the GND density and we have ignored the effect of other dislocation structures such as cell-size, cell-shape, SSDs, cell-wall misorientation etc. However it can be seen from the statistical analysis that under the current experimental conditions, GND density alone could satisfactorily represent the overall strength contribution due to dislocation structures. We attempted to use dislocation cell-size, to represent $D_{GNB}$ (in Equation 6.2) in the regression analysis. Cell-size was measured using EBSD analysis by changing the grain definition to 0.5° misorientation and substituted for GND density in the regression analysis. A large ‘$P$’ value was obtained for cell-size in the regression analysis indicating that the cell-size was not a major parameter influencing the yield stress of the alloy. This could be because of fairly constant cell sizes, in the range of 2.0-3.0 µm, obtained in all hot deformed samples. It is possible to obtain such an equilibrium cell-size during hot deformation and so the effect of applied stress during deformation will increase misorientation across cell-walls due to accumulation of dislocations, keeping cell-size relatively constant.

6.5.3. Determination of Coefficients

If we consider the average Taylor Factor as 2.73 (calculated for grains with cube orientation since the texture of 6022 alloy is predominantly cube), shear modulus ($G$) of 6022 alloy as 26 GPa and magnitude of Burger’s vector as $2.86 \times 10^{-10}$ m, the material constant $\alpha$ is determined to be 0.05. The material constant $\alpha$ is a function of strain rate
and temperature and when strengthening of materials is due to pure dislocation-dislocation interaction (without considering the effect of precipitates), the value of $\alpha$ is proposed to be 0.3 [7]. As expected, we obtained a lower value of $\alpha$ because of additional strength contribution due to dislocation-precipitate interactions included in the current analysis. Various yield strength models (regions of small strain) developed for Al alloys used $M$ value as 2, and they suggested that since the material is in early stages of plastic deformation, grains are not fully constrained and so the homogeneous stress hypothesis can be applied [13, 16]. Thus, reducing the value of $M$ to 2.0 will further increase the value of the material constant $\alpha$ to $\approx 0.1$.

6.6 Conclusions

The current work supports the trend of increasing interest in the scientific community towards quantifying the GND density in deformed samples and incorporating it into a physically based model. In general, the yield strength model developed for 6022 alloy is similar to the model proposed by Deschamps and Brechet [13]. Statistical analysis and experimental observations showed a linear relationship between yield stress and square root of GND density. It was observed that the samples with higher GND density show higher flow stress.
6.7 References

Chapter 7

7. Micromechanical Hardening of Elastic-Plastic Crystals Containing a Dilute Concentration of Elastic Inclusions

7.1 Introduction

In this chapter we propose a micromechanical model for elastic-plastic deformation of crystals containing elastic inclusions. The model is applicable for the simple case of dilute concentration of inclusions. It is based on a novel method for calculation of elastic strain energy associated with incompatible deformation of the matrix and the inclusion, whereby this energy is interpreted as the interaction energy of geometrically necessary dislocation loops (Mesarovic, S.Dj., *Int. J. Plasticity*, 21 (2005), 1855-89 [1]), which are geometrically equivalent to the incompatible strain. The method is general, easily applied to complex geometries and particle interactions, and – it often yields analytic solutions. The resulting model is remarkably simple; it falls within the framework of classical crystal plasticity with a specific elastic-plastic constitutive law that accounts for shape of inclusions.

7.2 Background

Motivated by their superior mechanical properties, a wide variety of inclusion-hardened materials, ranging from precipitation- and dispersion-hardened alloys to metal-matrix composites, have been developed during the past few decades. A variety of different inclusion sizes, volume fractions, shapes, and orientations can be produced by various processing routes.
Experimental investigations on the inclusion-hardened materials indicate that their mechanical properties are strongly dependent on the size, shape, spacing and orientation of the inclusions [2-6]. An example of variety in precipitate morphologies is shown in Figure 7.1. The needle type \( \beta'' \) precipitates in Al-Mg-Si alloys are oriented in the \(<100>\) direction of aluminum [7]. However, in Al-Cu alloys, the precipitates are disk-shaped and are oriented in the \(<100>\) direction of aluminum [8].

![Fig. 7.1](image)

Fig. 7.1) Bright Field TEM micrograph of microstructure of hardening precipitates. (a) Al-Mg-Si alloys. Small needle-shaped \( \beta'' \) precipitates are homogenously distributed in the matrix [7]. (b) Al-Cu alloys. The disk-shaped \( \theta' \) precipitates are seen in the microstructure [8].

The key to understanding the elastic-plastic deformation of inclusion-hardened crystals is the comparison with the inclusion-free crystal. In the former case, an additional work is required to deform a representative volume element (RVE) to the same strain. This additional work is stored as micro-elastic strain energy, arising from incompatible deformation of matrix and inclusion.
A number of phenomenological inclusion-hardening models have been suggested for both isotropic plasticity [2,8,9-11] and crystal plasticity [12-14]. The latter are based on the simplified expressions for the micro-strain energy using only the strain energy in the inclusion evaluated by Eshelby’s method [15].

In this chapter, we propose a general method for calculating the micro-elastic strain energy, based on Mesarovic’s [1] integral version of Kröner’s [16] continuum theory of dislocations. The model is applicable to any inclusion shape (albeit most conveniently applied to parallelepipeds) and may include inclusion interactions. It is easily generalized to include large inclusion rotations, as well as the distribution of shapes and sizes. In this chapter, we confine ourselves to the simplest case of non-interacting inclusions (dilute concentrations) and obtain simple closed-form solutions.

The chapter is organized as follows. In Section 7.3, we describe the general approach and formulation of the problem. In Section 7.4, a simple dislocation mechanics approach for calculation of micro-elastic strain energy is given and thus computed hardening incorporated into the theory. A summary and a brief discussion on model limitations and on future research is given in Section 7.5.

We use the following notation. Scalar quantities are given in italics, vectors, rank-two tensors and higher rank tensors are bold. The dyadic product of two arbitrary tensors is expressed by the symbol $\otimes$. Let $\mathbf{A}$ and $\mathbf{B}$ be rank 2 tensors, then $\mathbf{A} : \mathbf{B} = A_{ij} B_{ji}$ and $(\mathbf{A} \cdot \mathbf{B})_{ij} = A_{ik} B_{kj}$. Einstein notation with summation over repeated indices is used.
7.3 General formulation

We assume that deformation of inclusions is purely elastic. To simplify the algebra, we assume that the matrix and the inclusion have identical elastic properties.

Consider a virtual small displacement field \( \delta \mathbf{u} \), with the corresponding strain \( \delta \mathbf{\varepsilon} \). The principle of virtual work requires that the internal work of stresses \( \sigma \) over the volume \( V \) equals the external work of tractions \( t \) acting over the boundary \( S \):

\[
\int_V \sigma : \delta \mathbf{\varepsilon} \; dV = \int_S t \cdot \delta \mathbf{u} \; dS .
\] (7.1)

Presently, we discuss the linearized kinematics with infinitesimal strain and rotation and the consequent additive decomposition of elastic and plastic strain. In the more general context, finite deformation problems are decomposed into linearized increments. The present formulation can then be reinterpreted in terms of rates/increments in the sense of standard updated-Lagrangean formulation.

If the deformation is small, the strain tensor can be represented as the sum of the elastic strain \( \mathbf{\varepsilon}^e \) and the plastic strain \( \mathbf{\varepsilon}^p \). The symmetric plastic strain tensor \( \mathbf{\varepsilon}^p \) is the symmetric part of the slip tensor \( \mathbf{\gamma} \), which, in turn, is the weighted summation of the slips \( \gamma^\alpha \) on active slip systems \( \alpha \) \( (\alpha = 1, 2, \ldots) \):

\[
\mathbf{\varepsilon}^p = \text{sym}\{\mathbf{\gamma}\} = \sum_\alpha \gamma^\alpha \text{sym}\{\mathbf{s}^\alpha \otimes \mathbf{m}^\alpha\} .
\] (7.2)

Each slip system \( \alpha \) is defined by a par of unit vectors: unit vector normal to the slip plane \( \mathbf{m}^\alpha \) and a unit vector indicating the direction of slips \( \mathbf{s}^\alpha \). The principle of virtual work can then be written as

\[
\int_V \left( \sigma : \delta \mathbf{\varepsilon}^e + \sum_\alpha \varepsilon^\alpha \delta \gamma^\alpha \right) \; dV = \int_S t \cdot \delta \mathbf{u} \; dS .
\] (7.3)
Standard methods of variational calculus, applied to the weak form (7.3), lead to the yield condition, which states that the work-conjugate of slip, $\tau^\alpha$, must be equal to the resolved shear stress $\sigma : \left(s^\alpha \otimes m^\alpha\right)$.

The evolution law for $\tau^\alpha$ in a pure single crystal is usually written as

$$\delta \tau^\alpha = \sum_{\beta} h^{\alpha\beta} \delta \gamma^{\beta},$$

(7.4)

where $h^{\alpha\beta}$ are the work-hardening moduli for the inclusion-free crystal resulting from dislocation-dislocation interactions. Various models for $h^{\alpha\beta}$ have been suggested in the literature [17-20], based on experiments and statistical analysis of dislocation interactions. We will assume that the hardening moduli $h^{\alpha\beta}$ fully characterize the plastic deformation of the matrix.

As the simplest non-periodic we consider a matrix containing random distribution of small, non-interacting (widely-spaced), cuboidal inclusions (Fig. 7.2a). The representative volume element (RVE) with one inclusion is shown in Figure 2b.
Fig. 7.2) (a) Schematic representation of the representative volume element with volume $V_{RVE}$, (b) Cuboidal particle with volume of $V$.

The volume of the matrix, $V_M = V_{RVE} - V_\Omega$, is much larger than the volume of the particle $V_\Omega$. The volume fraction of a cubic inclusion in the RVE is

$$D = \frac{V_\Omega}{V_{RVE}} \quad \text{or} \quad D = \frac{8abc}{V_{RVE}}. \quad (7.5)$$

During elastic-plastic deformation of the RVE, the matrix $M$ deforms elastically and plastically but inclusion $\Omega$ deforms only elastically. To derive the appropriate constitutive relations, we can consider the deformation of an RVE to be a two-step process.

In the first step, assuming there is no strain incompatibility between $M$ and $\Omega$, the strain is uniform throughout the RVE. Thus, the overall strain of the RVE is equal to strain inside inclusion, $\varepsilon^{\Omega(1)}$, and strain in the matrix $\varepsilon^M(1)$:
\[ \varepsilon^{\Omega(1)} = \varepsilon^{M(1)} = \varepsilon^e + \text{sym}\{\gamma\}. \]  

(7.6)

The superscript (1) denotes the first step in the deformation process. The work done on the RVE in the first step, \( \delta W^{(1)} \), can be written as:

\[
\delta W^{(1)} = \int_{RVE} \left[ \sigma : \varepsilon^e + (1-D) \sum_{\alpha} \tau^{\alpha} \delta \gamma^{\alpha} \right] dV,
\]

where \( \sigma \) and \( \varepsilon^e \) are the stress and elastic strain in the RVE respectively. The term \( (1-D) \) in (7.7) implies that the plastic deformation is limited to the volume of the matrix, \( V_M \).

In the second step we introduce the stress-free eigenstrain \( \varepsilon^* \) [15] in the inclusion \( \Omega \) to compensate for the fictitious deformation that inclusion had suffered in the first step:

\[
\delta \varepsilon^* = -\text{sym}\{\delta \gamma\}.
\]

(7.8)

The second step is purely elastic and the work done \( \delta W^{(2)} \) is stored as the microstructural strain energy. The total work done on the RVE can be written as:

\[
\delta W = \int_{RVE} \left[ \sigma : \varepsilon^e + (1-D) \sum_{\alpha} \tau^{\alpha} \delta \gamma^{\alpha} \right] dV + \delta W^{(2)}.
\]

(7.9)

The microstructural strain energy is the quadratic form of the elastic strain field of the second step \( \varepsilon^{(2)}(x) \):

\[
\delta W^{(2)} = \int_{RVE} \varepsilon^{(2)}(x) : C : \delta \varepsilon^{(2)}(x) dV,
\]

(7.10)

where \( x \) is the position vector and \( C \) is the rank-four elastic tensor. The strain \( \varepsilon^{(2)}(x) \) can be considered to be proportional to eigenstrain \( \varepsilon^* \) by an arbitrary tensor field \( A(x) \) as,

\[
\delta \varepsilon^{(2)}(x) = A(x) : \delta \varepsilon^*.
\]

(7.11)
The microstructural strain energy (10) can then be written as

$$\delta W^{(2)} = \int_{\text{RVE}} \mathbf{F}^* \cdot \mathbf{F} \cdot \delta \mathbf{\varepsilon}^* \, dV,$$  \hspace{1cm} (7.12)

where $\mathbf{F} = \mathbf{A}(\mathbf{x}) : \mathbf{C} : \mathbf{A}(\mathbf{x})$. Then, since the eigenstrain is proportional to the slip tensor (7.8), we write:

$$\delta W^{(2)} = \int_{\text{RVE}} \mu : \text{sym}\{\delta \gamma\} \, dV,$$  \hspace{1cm} (7.13)

where the symmetric, rank-two tensor $\mu$ is the microstructural work-conjugate of $\text{sym}\{\delta \gamma\}$. The total virtual work can then be written as:

$$\delta W = \int_{\text{RVE}} \left[ \sigma : \delta \varepsilon^e + (1-D) \sum_{\alpha} \tau^\alpha \delta \gamma^\alpha + \sum_{\alpha} \mu : \left( s^\alpha \otimes m^\alpha \right) \delta \gamma^\alpha \right] \, dV.$$  \hspace{1cm} (7.14)

We can define the effective yield strength $T^\alpha$ for the slip system $\alpha$ :

$$T^\alpha = (1-D) \tau^\alpha + \mu : \left( s^\alpha \otimes m^\alpha \right)$$  \hspace{1cm} (7.15)

The evolution of resolved shear stress $\tau^\alpha$ follows the standard hardening law for crystals without inclusions (7.4), and thus the evolution of the effective yield strength can be written as

$$\partial T^\alpha / \partial \gamma^\beta = (1-D) k^{\alpha\beta} + \partial \mu / \partial \gamma^\beta : \left( s^\alpha \otimes m^\alpha \right).$$  \hspace{1cm} (7.16)

The Eq. (7.16) is the new hardening law for single crystals containing inclusions. The new principle of the virtual work now reads:

$$\int_{\text{RVE}} (\sigma : \delta \varepsilon^e + \sum_{\alpha} T^\alpha \delta \gamma^\alpha) \, dV = \int_S \mathbf{t} \cdot \delta \mathbf{u} \, dS.$$  \hspace{1cm} (7.17)

To fully define the new hardening law (7.16) the only term that needs to be determined is $\partial \mu / \partial \gamma^\beta$. If the microstructural work-conjugate $\mu$ is determined in terms of the amount
of slip in each slip plane, it can be substituted into (7.16), which completes the elastic-plastic constitutive equations. In the next section a simple method to calculate the microstructural work-conjugate $\mu$ is proposed.

### 7.4 Calculation of the microstructural work-conjugate $\mu_{ij}$

The microstructural work (7.10, 7.13) is the elastic strain energy arising from incompatible deformation of matrix and inclusion. This strain energy can be computed in more than one way. The often-used Eshelby’s method [15] is cumbersome and rarely provides analytic solutions required for derivatives in (7.16).

Recently, Mesarovic [1] showed that the microstructural energy is equivalent to the interaction energy of geometrically necessary dislocations represented by the Nye’s [21] dislocation density tensor. Moreover, Mesarovic derived integral formulae for direct computation of this energy that bypass the cumbersome computation of stress/strain fields that burden Eshelby’s and Kröner’s [16] formulations.

Simply put, the application of eigenstrain in Step 2 is equivalent to the introduction of geometrically necessary (GN) dislocation loops around the surface of inclusion. Figure 7.3a illustrates the case when the inclusion is subjected to the eigenstrain $\varepsilon_{i1}^*$. If $S_i^\pm$ represents for the face of inclusion perpendicular to the positive/negative direction of $x_i$ ($i=1,2,3$) axis, then the creation of dislocation loops around $S_2^\pm$, and $S_3^\pm$ is equivalent to the application of the eigenstrain $\varepsilon_{i1}^*$ in the inclusion (Fig. 7.3b). The burgers vector, $b_1$, is perpendicular everywhere to the dislocation line.
direction, $t_3$, and thus all the GN components are edge dislocations. In this case, the components of Nye’s dislocation density tensor can be written as:

$$
\alpha_{13} = -\varepsilon_{11}^* [\delta(x_2 + b) - \delta(x_2 - b)] \quad \text{for} \quad |x_2| < b; \quad (7.18a)
$$

$$
\alpha_{12} = -\varepsilon_{11}^* [\delta(x_3 + c) - \delta(x_3 - c)] \quad \text{for} \quad |x_3| < c. \quad (7.18b)
$$

![Diagram](image1)

**Fig. 7.3** (a) Application of the eigenstrain $\varepsilon_{11}^*$ in the particle. (b) Schematic representation of GN dislocation loops that are geometrically equivalent to eigenstrain $\varepsilon_{11}^*$.

The other components of the Nye’s dislocation density tensor vanish. The symbol $\delta$ represents the Dirac delta function, so that $\delta(x_2 + b)$ specifies the location of dislocation loops at the surface $S_2^-$. $\alpha_{13}$ is defined over the surfaces $S_2^+$ and $S_2^-$, and $\alpha_{12}$ is defined over the surfaces $S_3^+$ and $S_3^-$. Note that dislocations with burgers vector $b$ and
Fig. 7.4) (a) Application of the eigenstrain $\varepsilon_{12}^*$ in the particle. (b) Schematic representation of GN dislocation loops that are geometrically equivalent to eigenstrain $\varepsilon_{12}^*$.

The equivalent dislocation loops corresponding to $\varepsilon_{12}^*$ are shown in Figure 7.4.

The non-vanishing components of the Nye’s tensor are

\[
\begin{align*}
\alpha_{13} &= -\varepsilon_{12}^* [\delta(x_1 + a) - \delta(x_1 - a)] & \quad |x_1| < a; \\
\alpha_{11} &= -\varepsilon_{12}^* [\delta(x_3 + c) - \delta(x_3 - c)] & \quad |x_3| < c; \\
\alpha_{32} &= -\varepsilon_{12}^* [\delta(x_2 + b) - \delta(x_2 - b)] & \quad |x_2| < b; \\
\alpha_{22} &= -\varepsilon_{12}^* [\delta(x_3 + c) - \delta(x_3 - c)] & \quad |x_3| < c.
\end{align*}
\]
Note that $\alpha_{13}$ and $\alpha_{32}$ represent edge dislocations, while $\alpha_{11}$ and $\alpha_{22}$ represent screw dislocations.

![Diagram](image)

Fig. 7.5) Schematic representation of GN dislocation loops that are geometrically equivalent to eigenstrains $\varepsilon_{11}^*$ and $\varepsilon_{23}^*$.

When a combination of eigenstrains $\varepsilon_{11}^*$ and $\varepsilon_{23}^*$ is applied, the resulting equivalent dislocation loops are shown in Figure 7.5. In this case the non-vanishing components of Nye’s dislocation density tensor are

\begin{align}
\alpha_{13} &= -\varepsilon_{11}^* [\delta(x_2 + b) - \delta(x_2 - b)] \quad |x_2| < b; \quad (7.20a) \\
\alpha_{12} &= -\varepsilon_{11}^* [\delta(x_3 + c) - \delta(x_3 - c)] \quad |x_3| < c; \quad (7.20b) \\
\alpha_{21} &= -\varepsilon_{23}^* [\delta(x_2 + b) - \delta(x_2 - b)] \quad |x_2| < b; \quad (7.20c) \\
\alpha_{22} &= -\varepsilon_{23}^* [\delta(x_1 + a) - \delta(x_1 - a)] \quad |x_1| < a; \quad (7.20d) \\
\alpha_{13} &= -\varepsilon_{23}^* [\delta(x_3 + c) - \delta(x_3 - c)] \quad |x_3| < c; \quad (7.20e)
\end{align}
\[ \alpha_{33} = -c_{23}^* [\delta(x_3 + a) - \delta(x_3 - a)] \quad \text{if } |x_3| < a. \tag{7.20f} \]

In reality, geometrically necessary dislocations are spread across a thin boundary layer at the interface. For the purpose of energy calculation, we approximate the boundary layer by placing all GN dislocations at the interface. In Section 4, we address the validity of this approximation in more detail.

In the presence of GN dislocations, an additional microstructural work, \( \delta W_m \), is required to deform the material to the same strain as a putative GN dislocation-free crystal. On the macroscopic, continuum level, this work is identified with the strain energy associated with incompatibility. On the microscopic, dislocation mechanics level, the microstructural work was identified with the sum of the interaction energy among GN dislocations and boundaries and is a functional of Nye’s dislocation density tensor [1]. Formally, it is written as a double convolution over the volume with non-vanishing Nye’s densities (and is therefore non-local):

\[
W_m = \frac{1}{2} \int_V \int_{V'} M_{jkpq}(x' - x)\alpha_{jk}(x)\alpha_{pq}(x')dV'dV. \tag{7.21}
\]

The double integration is over the volume \( V = V' \), and \( x \in V, x' \in V' \) are respective position vectors.

where \( x \) and \( x' \) are the position vector of two dislocation loop points, and \( \alpha_{ij} \) represents the component of the Nye’s dislocation density tensor.

The components of the two-point, rank-four tensor \( M \) are

\[
M_{jkpq} = \frac{2\mu}{8\pi R} \left( 2\delta_{kp}\delta_{jq} - \delta_{jk}\delta_{pq} \right) + \frac{E}{8\pi R} \varepsilon_{ijk}\varepsilon_{mpq} (\delta_{im} - d_i d_m), \tag{7.22}
\]
where $\delta_{kp}$ are the Kronecker deltas and $\epsilon_{ijk}$ is the permutation symbol. $\mu$ is the shear modulus, $\overline{E} = 2\mu /\nu$ is the plane strain modulus and $\nu$ is the Poisson ratio. The unit direction vector $d$ is

$$d = R/R,$$  \hspace{1cm} (7.23)

where $R$ is the magnitude of the relative position vector $R = x' - x$.

The components of $\mathbf{M}$ satisfy $M_{jkpq} = M_{pqjk}$. When eigenstrain $\epsilon^*_{11}$ is applied, the non-vanishing components are $M_{1312}$, $M_{1313}$ and $M_{1212}$. When eigenstrain $\epsilon^*_{12}$ is applied, $M_{1111} = M_{2222} = \mu /4\pi R$, $M_{1122} = -M_{1111}$, while $M_{1313}$, $M_{3232}$ and $M_{1332}$ are functions of $d$. Since the interaction energy of edge and screw dislocations vanishes:

$$M_{1113} = M_{1132} = M_{2213} = M_{2232} = 0.$$

Upon substitution of $\alpha_{ij}$ (7.18, 7.19, 7.20) and $M_{jkpq}$ (7.22) into (7.21), the microstructural energy $W_m$ is computed by direct integration. The total microstructural energy $W_m$ can then be written as

$$W_m = \frac{1}{2} \mathbf{e}^*: \mathbf{P} : \mathbf{e}^*,$$ \hspace{1cm} (7.24)

where the rank-four tensor $\mathbf{P}$ is computed by integrating (7.21). For non-interacting inclusions, its components are functions of inclusion dimensions, $a, b, c$, only. The non-vanishing components of $\mathbf{P}$ are given in the Appendix. Owing to the symmetries of cuboidal particle and non-interaction of edge and screw dislocations, most components of $\mathbf{P}$ vanish. This can be explained by the symmetric configuration in the case of cubic inclusion. Thus, the microstructural energy is a function of eigenstrain and particle dimensions:
\[ W_m = W_m(\varepsilon^s, a, b, c) \]  

(7.25)

Upon dividing (7.24) by (7.5) and substituting (7.8) into (7.24), the microstructural energy density, \( w_m \), is written as

\[ w_m = \frac{1}{2} \text{sym}\{\gamma\} : P(\bar{\alpha}, \bar{\beta}, \bar{\gamma}) : \text{sym}\{\gamma\}, \]  

(7.26a)

with non-dimensional parameters:

\[ \bar{\alpha} = aD^{1/3}/(8abc)^{1/3} \, , \, \bar{\beta} = bD^{1/3}/(8abc)^{1/3} \, , \, \bar{\gamma} = cD^{1/3}/(8abc)^{1/3}. \]  

(7.26b)

Then, from (13), the microstructural work-conjugate \( \mu \) can be obtained as:

\[ \mu = \partial w_m / \partial \text{sym}\{\gamma\} = P(\bar{\alpha}, \bar{\beta}, \bar{\gamma}) : \text{sym}\{\gamma\}. \]  

(7.27)

The final form of the new hardening law for the crystals containing elastic inclusions is then obtained as

\[ \partial T^\alpha / \partial \gamma^\beta = (1 - D)h^{\alpha\beta} + \Delta h^{\alpha\beta}, \]  

(7.28a)

where, using the symmetries of \( P \):

\[ \Delta h^{\alpha\beta} = \left( s^\beta \otimes m^\beta \right) : P : \left( s^\alpha \otimes m^\alpha \right) \]  

(7.28b)

The hardening moduli \( h^{\alpha\beta} \) correspond to the dislocation-dislocation interactions assumed to be the same as those in the inclusion-free crystal. The additional hardening \( \Delta h^{\alpha\beta} \) is the result of incompatible deformation of matrix and inclusion.
7.5 Summary and discussion

The micromechanical model for elastic-plastic deformation of crystals containing elastic inclusions is based on a novel method for calculation of elastic strain energy associated with incompatible deformation of the matrix and the inclusion, whereby this energy is interpreted as the interaction energy of geometrically necessary dislocation loops [1] which are geometrically equivalent to the incompatible strain. The method is general and easily applied to complex geometries. For the simple case of dilute concentration of inclusions the method is remarkably simple; analytic solutions for microstructural strain energy are easily computed and the resulting model falls within the framework of classical crystal plasticity with a specific elastic-plastic constitutive law that accounts for shape of inclusions.

The only assumption used in the above derivation is that the GN dislocations – in reality spread across a thin boundary layer, are packed at the interface. The computed energy approximates the actual energy well as long as the width of the boundary layer, $\lambda$, is much smaller than the dimension of the particle in the direction normal to the interface, $L$, as shown in Figure 7.6. If, on the other hand $\lambda/L \geq 1$, the interaction energy is strongly dependent on the actual distribution of dislocation [1].
Fig. 7.6) The schematic diagram of a Nye’s dislocation density component representing a pile-up of dislocations. (a) The boundary layer thickness, $\lambda$, is small relative to the particle thickness, $L$. (b) The boundary layer consisting of dislocations piled-up against a thin particle, $\lambda/L \geq 1$. 
The major advantages of the present model over the previous proposals based on Eshelby’s solution [12-14] are: its simplicity, accuracy and clear micromechanical foundation. The latter allows for reasonable error estimates and the extensions to more complex problems. The major steps in future development are as follows.

The resulting effective microstructural hardening law (7.28) is linear. Such behavior has been observed at early stages of deformation ([22], Fig. 9, for 1/3% concentration of SiO₂ particles in copper.) At later stages of deformation, dislocations will cross slip at the boundary layer and the back-stress from boundary layers will impede the sources [22], resulting in the effective saturation of boundary layers and the breakdown of the linear hardening low. These effects are currently not included into the model, but simple corrections based on the cross slip calculations at the edge of the particle may suffice. This would amount to effectively putting a limit on the microstructural slip work-conjugate, µ (7.15), on the basis of the double cross slip at the edge of the boundary layer.

The interactions of particles (for dense concentrations) pose no conceptual problem in the present framework. To gauge the effects of particle interactions, one may consider a periodic array of particles. The computations for the constitutive tensor P (7.28, Appendix A) now involve infinite summations over periodic arrays followed by integration (7.21). Since the GN dislocations at opposing sides of a particle form superdipols, the infinite sums are alternating and convergent. Extension to finite deformation and the effects of finite particle rotation pose no conceptual difficulties. In the first instance, the present framework is interpreted as rate/incremental formulation, with appropriate updates of the geometry between the increments.
7.6 References


Chapter 8

8. Contribution of This Work

Better understanding of the physics of deformation and structure development will result in the opportunity to reduce alloy content, minimize processing steps (such as annealing treatments), and improve performance of existing products. The ultimate goal of this research is to develop an integrated methodology for modeling the deformation behavior of Al alloys based on microstructural evolution to achieve the above mentioned opportunities. In the literature, a large number of constitutive equations describing the plastic behavior of materials are available for materials modeling applications. However, the applicability of commonly used constitutive equations is usually limited in terms of both processing parameters including strain, strain rate and temperature, and the evolution of microstructural features including dislocation structures, precipitate morphologies and grain characters.

It is well established that deformation behavior of a material is a function of its microstructural features, and thus, a crucial aspect of the modeling is to understand the microstructure-property relations. This requires systematic individual effort in the area of microstructural characterization, understanding the influence and importance of microstructural parameters, and development of constitutive equations based on the most important microstructural parameters. This research is mainly focused on experimental characterization and multiscale modeling of the microstructure – property relationship in precipitation hardening aluminum alloys. The main contribution of the present research is in the areas of understanding the details of precipitation-dislocation interactions, determining the significance of these interactions on the flow stress response, and
developing a multiscale model which is based on the interaction of dislocations and precipitates.

To study the interaction of precipitation and dislocations, it is important to have a good understanding about the morphology and precipitate types which may exist in a precipitation hardening alloy, such as AA6022. Moreover, this study was highly in demand for automotive manufacturing companies, because of the application of this alloy to automotive body panels. In body panel sheet materials two important properties are in demand, the formability and the strength. These two properties often have adverse effects on each other, and sometimes result in the formation of cracks during manufacturing. Figure 8.1 shows an example of failure during the Hemming process, bending over 180 degrees, of AA6022 [1]. To optimize formability and strength of AA6022, one has to understand the precipitate morphology of the alloy. Although the precipitation reactions in Al-Mg-Si alloys have been studied extensively, details of the precipitation sequence in aluminum alloy 6022 have not yet been fully understood. Hence, the first step of this research project was devoted on identification of the precipitates and understanding the details of precipitation sequence.
In Chapter 3, a systematic combination of differential scanning calorimetry and transmission electron microscopy was used as the major characterization techniques to identify the precipitate structures of this alloy. It was found that at early stages of ageing there are some unknown small precipitates which form prior to the formation of $\beta''$ precipitates and these were not reported in the previously suggested precipitation sequence for this alloy. These small precipitates form in the range of the paint baking process (~30 min at 175°C) of this alloy and should be considered for any further alloy modifications required to increase the formability of this alloy. Moreover, this study resulted in identification of a new precipitation sequence in this alloy. As a future work, this information can be combined with bending and tensile experiments to better understand the influence of each one of these identified metastable phases on formability.
and strength properties. This study is beyond the scope of this research project, and should be followed in a separate study.

To achieve the objective of this research, i.e. understanding the interaction between dislocations and precipitates, the next logical step after identification of precipitation sequence, is to study the influence of dislocation structure on precipitation reaction and the influence of precipitate morphology on dislocation structure development. Considering that deformation prior to aging has been used in industry as a tool to influence the aging behavior of Al-Mg-Si alloys, this information is also highly useful for understanding the details of decomposition in deformed state. Understanding the influence of dislocations on precipitation was achieved by a systematic combination of TEM and DSC measurements on predeformed specimens which were discussed in Chapter 4. In this study, selected samples were subjected to deformation prior to aging and the precipitation sequence was compared with those in undeformed state. The results showed that the precipitation sequence and morphology were considerably affected by deformation prior to aging. It was observed that the formation of Q’ was promoted in the presence of dislocations. This is quite unexpected, considering that both Q’ and β’ have hexagonal crystal structure. This can be explained in terms of crystallographic orientation of these two phases. The habit plane of Q’ is \{150\} of the aluminum matrix [2], and the repeat distance along the \<150> directions of the aluminum matrix is 1.03 nm which is about the same as the lattice parameter of the Q’ phase. Therefore the precipitates tend to form as a lath so as to minimize the misfit in its surface and hence its energy. Also the DSC data were used to study the kinetics of precipitation in the presence of dislocations.
The results show that dislocations facilitate precipitation by decreasing the activation energy.

After investigating the influence of dislocations on precipitation, subsequently the effect of precipitates on dislocation structures was studied by a combination of OIM and TEM, and was discussed in Chapter 5. In this work, two different precipitate types were distributed homogenously in 6022 alloy specimens, and then subjected to deformation up to 10%. After deformation the orientation measurements were performed by the EBSD technique. Since the most important quantity that describes dislocation structures is dislocation density, an extra work was required to extract the dislocation density information. Thus, in a separate study by Trivedi [3], a code was developed to determine the spatial distribution of dislocations using the lattice curvature information from EBSD. In this approach, Nye’s formulation was implemented in order to link the measured orientation gradients to the dislocation densities [4]. These dislocations are required to accommodate lattice curvature and thus called geometrically necessary (GN) dislocations. Our detailed analysis indicates the significant influence of precipitate morphology on GN dislocation densities. It was found that the stronger the precipitates, the higher the lattice rotations and thus the higher the densities of GN dislocations. The study showed that the evolution of GND density depends on the interaction between precipitates and dislocations, which in turn is governed by the precipitate morphologies of the starting microstructure. Evidently the statistically stored dislocations were ignored in this study. This would not diminish the interpretation of results since in Chapter 6 we showed that the flow stress of the material scale well with GN dislocations and thus their evolution can represent the evolution of total dislocation density.
The overall experimental results clearly indicate that the evolution of both dislocations and precipitates depends on each other and their interaction should be considered in materials modeling. Therefore, in the first step for materials modeling, it is much simpler to develop a phenomenological internal state variable model for the flow stress based on the interaction of dislocations and precipitates. In addition, the derivation of a phenomenological model and understanding the type of dependence of flow stress to the microstructural variables is necessary to develop more sophisticated physical based models. To develop a phenomenological model for flow stress, it is necessary to understand the degree of influence of the precipitate and dislocation parameters on the flow stress behavior of the material. To achieve this, using hot deformation a various precipitate morphologies and dislocation structures were produced as a starting microstructure (Chapter 6). A parametric study was performed using multiple regression analysis to determine relative influence of various microstructural parameters on the flow stress of 6022 Al alloy. The analysis showed that average value of GN dislocation density was the major parameter, and particle geometries were the two most effective parameters on the flow stress behavior of 6022 Al alloy. The strong dependence of the GND density on the observed stress response further motivated the interest of developing a relationship between the GND density and the yield stress of 6022 Al alloy. Statistical analysis and experimental observations showed a linear relationship between yield stress and the square root of GND density. Also the relationship developed between microstructure and yield stress was similar to the model proposed by Deschamps and Brechet [5]. Another interesting feature of the study is that only geometrically necessary dislocation density measured in 2-D plane section of the sample is used in the model and experimental
analysis. Still, the relationship between dislocation density and yield stress is retained even though statistically stored dislocation density and the gradient of orientation in the third direction is ignored.

The previous study showed that the interaction of GN dislocations and precipitates strongly affects the flow stress behavior of material. Therefore the next logical step is to incorporate these interactions in the constitutive equations governing the flow stress. To achieve this we used an energy method to take into account the interaction of GN dislocations and precipitations. To avoid complex mathematical treatments, we assumed dilute concentration of precipitates where the precipitates remain elastic during plastic deformation. The details of this study are discussed in Chapter 7. The resulting micromechanical model is remarkably simple, and falls within the framework of classical crystal plasticity with a specific elastic-plastic constitutive law that accounts for the shape of inclusions.

Overall the current study claims to make contribution in the areas of precipitation sequence analysis, dislocation precipitation interactions, identification of major microstructural parameters affecting stress response, and developing a phenomenological model for the yield stress and a micromechanical model based on the interaction of precipitates and GN dislocations. The interaction of precipitates and dislocations were studied in details. This study showed that the evolution of precipitates and dislocations is correlated and it is more realistic to consider both in materials modeling. A parametric study determined the degree of influence of precipitate and dislocation characteristics and this information was used to develop a phenomenological model based on the interaction of precipitates and dislocations. Eventually, a simple micromechanical model was
developed to incorporate the interaction of precipitates and dislocations into the constitutive equations of plastic deformation of single crystals.

8.1 References


Chapter 9

9. Conclusions

In this dissertation the interaction between precipitates and dislocations in AA6022 was investigated by means of DSC, TEM, EDS, EBSD, and hardness measurements. In the first step, the precipitation sequence in AA6022 was studied during isothermal and dynamic aging scenarios. Our detailed analysis revealed the presence of small unknown precipitates prior to the formation of $\beta''$ precipitates which was not reported earlier. These precipitates form in the range of the paint baking process (~30min at 175°C) of this alloy and should be considered for any further alloy modifications required to increase the formability of this alloy. It was found that some of the $\beta''$ needles transform during growth to lath-shaped precipitates which are likely one of the $Q'$ precursors. We proposed the following precipitation sequence in AA6022:

Clusters / GP zones $\rightarrow$ small precipitates $\rightarrow \left\{ \begin{align*} \beta'' &\rightarrow \beta' \\ \beta'' &\rightarrow \text{Lath shaped precipitates} \rightarrow Q' \rightarrow \beta + \text{Si} \end{align*} \right.$

The effect of dislocations on the precipitation reactions of an Al-Mg-Si alloy (AA6022) was also investigated. Thermal analyses were performed on DSC data to extract the kinetic information of precipitation reactions. It was found that deformation prior to aging resulted in decrease of activation energy required to $\beta''$ formation. It was seen that presence of dislocations changed the character of precipitates from $\beta''$ to $\beta' + Q'$. Another major finding of this research corresponds to the influence of dislocations on the formation of $Q'$. It was found that at higher temperatures only $Q'$ precipitates were present in the microstructure of the predeformed samples. It was concluded that the $Q'$
precipitates are more likely to form by heterogeneous nucleation processes. In this vein the precipitation sequence in deformed state can be written as below:

$$\text{Clusters} / \text{GP zones} \rightarrow \beta' + Q' \rightarrow Q'$$

In the aspect of influence of precipitates on dislocations, our results indicated a clear dependency of GND and orientation distribution within the individual grains on the character of precipitates. It was shown that the presence of the semi-coherent $\beta''$ precipitates associated with the peak-aged condition resulted in significant increase in GND density and local misorientation within the grains. However these effects were insignificant for the $\beta'$ and $Q'$ associated with the overaged condition.

The parameters corresponding to precipitates and dislocations were incorporated in a phenomenological yield stress model as additive terms which represent the most simplest scenario for precipitate and dislocation interactions. The model is relatively simple and obtained based on regression analysis. Statistical analysis and experimental observations showed a linear relationship between yield stress and square root of GND density. It was observed that with the increasing the GND density content of the alloy, the flow stress was higher. This result is in favor of materials modelers who try to quantify the GND density in deformed samples and incorporating it into a physically based model.

Eventually, the interaction of precipitates and dislocations was modeled in the framework of crystal plasticity which is applicable for the computational materials scientists. The parameters related to GNDs and precipitate shapes were used to establish a micromechanical model based on the rigorous calculation of elastic strain energy associated with the GND loops around the precipitates. For the simple case of dilute
concentration of precipitates the method is remarkably simple; analytic solutions for microstructural strain energy are easily computed and the elastic-plastic constitutive law accounts for shape of precipitates.
Chapter 10

10. Suggestions for Future Work

The precipitation and dislocation analysis performed in this work can be coupled with formability tests in order to correlate the formability properties as a function of precipitate and dislocation characters. Tailoring formability by specifying a process path and then monitoring the evolution of the microstructure features including dislocation cell structures, precipitate morphology and crystallographic texture can lead to insightful information useful for auto-makers. The relative influence of this microstructural information can be carefully analyzed by available statistical tools such as ANOVA. In addition, proper correlating microstructural features to formability will assist us in developing more advanced internal state variable models useful for materials multi-scale modelers.

The influence of predeformation on precipitate reactions of AA6022 discussed in Chapter 4 was concerned with small strain-rate deformation process. In a complementary work, we studied the impact of high strain-rate deformation, shock-loading, on the precipitation sequence and aging behavior of AA6022 by means of DSC, TEM and hardness measurements. This work has been discussed in details in Appendix B of this dissertation.

In Appendix C, we describe a new approach for modeling the age-hardening behavior of Al-Mg-Si alloys that utilizes artificial neural networks (ANN) models to connect key microstructural parameters for realistic precipitate morphologies with the age-hardening response. The ANN modeling is a phenomenological approach that provides us with a better understanding on the degree of significance of each input
variable. Such studies on the parameters related to the interaction of precipitates and
dislocations will be beneficial to materials modeler societies.

The phenomenological modeling of GNDs evolution is another suggestion of the
author. Although the importance of GNDs in materials deformation has been discussed
for many years, in the literature one can not find a proper evolution equation for the
GNDs. Recent advancements in automated EBSD and high resolution electron
microscopes have enabled us to study the local variation of orientation within the grains
and correlate this to GND densities. Therefore, it is logical to experimentally study the
evolution of GNDs as a function of grain orientation, neighboring grain, and precipitate
characters in order to estimate this evolution by a phenomenological model. This model
can be joined with the framework of a physically based model to study more accurately
the materials response during deformation.

The micromechanical model derived in this work is applicable for dilute
concentration of precipitates and obviously the interaction effect of precipitates has been
ignored. It is more realistic to consider that the precipitates interact with each other until
some extents. The interaction effect of precipitates distributed in a periodic manner can
be captured similar to the atomistic approximations. The relative interaction energy can
be estimated for the nearest neighborhoods and be added to the microstructural work
necessary to accommodate deformation in precipitation hardening materials. In addition,
the crystal plasticity model developed in this work can be extended to finite deformation
formulation if the relative orientation evolution of precipitates and crystal lattice during
deformation is captured.
Appendix A: Components of P Matrix

To derive the constitutive tensor $\mathbf{P}$ discussed in Chapter 7, we have used the commercial symbolic manipulation code Mathematica\(^1\). The $P_{1111}$ and $P_{1212}$ components of $\mathbf{P}$ tensor are calculated by (7.21) and (7.22), and are given in this Appendix. The rest of components can be obtained by permutation rule. Note that $\log(x)$ represents the natural logarithm of $x$.

\[
\begin{align*}
R_{1111} &= \frac{E}{\pi} \left( \frac{1}{3} \left[ 4a^3 - \frac{41}{2} (b^3 + c^3) - 4(a^2 - 5b^2)\sqrt{a^2 + b^2} - 4(a^2 - 5c^2)\sqrt{a^2 + c^2} + 20(b^2 + c^2)^{3/2} \right] \\
&\quad + 4(a^2 - 5b^2 - 5c^2)\sqrt{a^2 + b^2 + c^2} \right) + 16abc \left( \arctan \left( \frac{ab}{\sqrt{a^2 + b^2 + c^2}} \right) + \arctan \left( \frac{ac}{b\sqrt{a^2 + b^2 + c^2}} \right) \right) \\
&\quad + \frac{4ab^2 \log}{-a + \sqrt{a^2 + b^2 + c^2}} \left( \frac{a + \sqrt{a^2 + b^2 + c^2}}{a + \sqrt{a^2 + b^2}} \right)^2 \frac{b}{\sqrt{b^2 + c^2}} \\
&\quad + \frac{2ac^2 \log}{-c + \sqrt{a^2 + b^2 + c^2}} \left( \frac{c + \sqrt{a^2 + b^2 + c^2}}{c + \sqrt{a^2 + b^2}} \right)^2 + 2ba^2 \log \left( \frac{-b + \sqrt{a^2 + b^2 + c^2}}{b + \sqrt{a^2 + b^2 + c^2}} \right) \\
&\quad + \frac{6bc^2 \log}{-b + \sqrt{a^2 + b^2 + c^2}} \left( \frac{c + \sqrt{a^2 + b^2 + c^2}}{c + \sqrt{a^2 + b^2}} \right)^2 -c + \sqrt{a^2 + b^2 + c^2} \\
&\quad + \frac{2bc^2 \log}{-b + \sqrt{a^2 + b^2 + c^2}} \left( \frac{-c + \sqrt{a^2 + b^2 + c^2}}{-b + \sqrt{a^2 + b^2 + c^2}} \right) \\
&\quad + \frac{2bc^2 \log}{-b + \sqrt{a^2 + b^2 + c^2}} \left( \frac{-c + \sqrt{a^2 + b^2 + c^2}}{-b + \sqrt{a^2 + b^2 + c^2}} \right) \\
&\quad + \frac{2bc^2 \log}{-b + \sqrt{a^2 + b^2 + c^2}} \left( \frac{-c + \sqrt{a^2 + b^2 + c^2}}{-b + \sqrt{a^2 + b^2 + c^2}} \right)
\end{align*}
\]

\[ P_{1212} = \frac{4E}{3\pi} \left( 12a^3 + 12b^3 - 2c^3 - 12U^{3/2} - 6(2a^2 - c^2)V - 6(2b^2 - c^2)W + 6(2a^2 + 2b^2 - c^2)Z + \right. \\
\left. 6ca^2 \log \left( \frac{-c + Z}{c + Z} \right) \left( \frac{c + V}{-c + V} \right) \right) + 6cb^2 \log \left( \frac{c + W}{c + Z} \right) \left( \frac{-c + Z}{-c + W} \right) \left( \frac{U}{b} \right) \right] + \\
\left. 6ca^2 \log \left( \frac{a^2 V^2 + 2c^3 (c + V)}{4a^2 + 2W^2 + c^2 (b^2 + 2c(c + Z))} \right) \left( \frac{U}{a} \right)^2 \right) + \\
\frac{4\mu}{3\pi} \left( -4a^3 - 4b^3 + 8c^3 + 4a^2 (U + V - Z) + 4b^2 (U + W - Z) - 8c^2 (V + W - Z) - 24abc ArcTan(\frac{ab}{cZ}) - \right. \\
\left. 6ab^2 \log \left( \frac{-a + Z}{a + Z} \right) \left( \frac{a + U}{-a + U} \right) \right) - 6ba^2 \log \left( \frac{b + Z}{b + Z} \right) \left( \frac{b + U}{-b + U} \right) + \\
\left. 6ab^2 \log \left( \frac{-a + Z}{a + Z} \right) \left( \frac{a + V}{-a + V} \right) \right) + 6bc^2 \log \left( \frac{b + Z}{b + Z} \right) \left( \frac{-b + W}{b + W} \right) + 24bc^2 \log \left( \frac{b + W}{b + Z} \right) \left( \frac{V}{c} \right) \right) \]
Appendix B: The Effect of Shock-Loading on the Aging Behavior of an Al-Mg-Si Alloy

B.1. Introduction

The influence of predeformation on precipitate reactions of AA6022 discussed in Chapter 4 was concerned with small strain-rate deformation process. In a complementary work, we studied the impact of high strain-rate deformation, shock-loading, on the precipitation sequence and aging behavior of AA6022 by means of DSC, TEM and hardness measurements. The samples were solutionized and quenched in water prior to subsequent shock-loading and aging treatment. The TEM and DSC results show that, while shock-loading prior to aging facilitates the precipitation of Q’ and β, no significant effect on β’ precipitates was observed. The hardness studies indicate that pre-shock loading strengthens the material by forming a high concentration of microstructural defects, however the resultant mechanical properties of the shocked sample are comparable to those without shock processing at the peak of aging. It was found that the rate of overaging is higher in shocked samples, which is in agreement with the DSC and TEM results.

B.2. Background

The relationship between intense shock compression and material defects has had a long history, dating back to the early work of C.S. Smith [1] who proposed a specific mechanism for the generation of dislocations occurring at moving shock discontinuities. Early work on dynamic yielding resulting in elastic precursor decay (Asay et al. [2])
illustrated the significant effects of small preexisting concentrations of divalent impurities on dynamic yield processes in single crystal LiF. Generally, it is known that shock-loading produces a large number and variety of distributed defects in solids, including dislocations, stacking faults, and twins. An extensive literature has been developed dealing with the effects of shock-loading on the production of these various defects that are known to influence mechanical properties such as quasi-static loading. It is not appropriate to discuss this previous work in the present chapter; the reader is directed to a few selected references for further information on the topic (Meyers [3], Murr [4], Gray [5], Davison and Graham [6], Murr [7]). In contrast to the general studies of shock-induced defects, there are relatively few reports dealing with the effect of shock-loading on the specific issue of aging properties resulting after shock-loading. Recent papers on this issue include the work of Esquivel and Inal [8] on the characterization of a shock-loaded aluminum alloy, Uvarov et al. [9] on the effect of shock-wave prior to the aging of austenitic stainless steels, and Bekrenev and Naumov [10] on studies of aging processes in shocked aluminum alloys.

In spite of a limited number of studies on the combination of shock-loading and aging response of aluminum alloys, apparently no detailed analyses are available on the effect of shock-loading on the evolution of precipitation structures of these alloys during aging. In contrast, extensive studies on the precipitation sequence of aluminum alloys without shock-loading are available in the literature [e.g. 11-13]. In general, the age-hardening response of Al-Mg-Si alloys is based on the precipitation reactions. A widely accepted precipitation sequence in these alloys is:

\[ \alpha \text{(SSSS)} \rightarrow \text{Clusters/GP zones} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta \]
Atomic clusters of Mg and Si and GP zones are believed to form at an early stage of precipitation from supersaturated Al-Mg-Si aluminum alloy [11-13]. Their existence has been confirmed by means of three dimensional atom probe analyses (3DAP) [12]. The $\beta''$ are fine needle shaped precipitates along $<100>_{\text{Al}}$ and have monoclinic structure [14]. Maximum hardness can be achieved when $\beta''$ dominates the precipitates in the material. The $\beta'$ precipitates with hexagonal crystal structure form after $\beta''$ precipitates in the aging sequence [15]. They are rod-shaped and are aligned along $<100>_{\text{Al}}$. In Al-Mg-Si alloys, the equilibrium $\beta$–phase has antiflourite FCC structure with lattice parameter of 0.639nm [16].

This chapter aims to investigate the effect of shock-loading on the precipitation sequence during dynamic aging and isothermal aging of an Al-Mg-Si alloy. It is expected that the production of a high and uniform concentration of microstructural defects due to shock-loading influence the aging response of the material. In this work systematic TEM and DSC experiments were performed to characterize the evolution of precipitate structures as well as aging response of an Al-Mg-Si alloy.

**B.3. Experimental Plan**

Aluminum alloy 6022 was received in thin plate form with a thickness of 3.07 mm. Solution treatment was carried out at 550°C for 1 hour with a programmable furnace and then water-quenched to room temperature. The samples were then preserved at 0°C before further experiments.
Fig. B.1) Experimental configuration used for shock-loading and soft recovery of aluminum samples shocked to about 2.3 GPa. The inside of the soft recover fixture was filled with absorbent materials to minimize secondary loading of the recovered aluminum sample after impact and release from the guard ring.

A schematic of the impact test and soft recovery configuration of samples is shown in Fig. B.1, which is based on designs previously developed [17,18]. For experiments of shock-induced aging effects, 6022 aluminum samples were machined in the form of disks, 50.8 mm in overall diameter and 3.07 mm in thickness. Each sample studied was prepared in two pieces. The inner piece was 25.4 mm in diameter with a beveled edge on the outer diameter of 8 degrees to the normal. The outer ring had a matching bevel angle to accommodate the inner piece with a tight press fit between the inner diameter of the ring and the central piece. The bevel angle direction was chosen, as illustrated in Fig. B.1 to allow quick separation of the central aluminum sample from the aluminum guard ring after first shock passage and consequent unloading upon reflection for the shock wave from the back surface (right side in Fig. B.1) of the sample assembly.
The inner diameter was designed so that after the central piece is fully unloaded, the inward moving radial release waves would cause a separation of the two pieces, resulting in a central piece which was only loaded and unloaded with planar stress waves. The pieces were bonded together with a molybdenum lubricant to minimize perturbations caused by the shock wave at this interface. To produce the desired impact stress, the sample was impacted by a flat disk of aluminum accelerated to the velocity of 292 m/s. A measured planar impact stress of about 2.3 GPa was produced upon initial impact and maintained for a time duration of about 1 \( \mu \)s before planar unloading by shock reflection from the back free surface of the sample. Immediately after the shock wave experiment, the sample was recovered from the recovery fixture and placed in a liquid nitrogen bath for further metallurgical examination.

To perform DSC experiments, the shock loaded samples were grinded on both surfaces to the thickness of 0.5mm and then punched into 3mm disks. The average weight of the DSC samples was 9.4±0.3 mg. The Rheometric Scientific\textsuperscript{TM} DSC instrument was used for calorimetric analyses. A protective atmosphere of pure argon at the rate of 11 ml/min was passed through the cell to avoid materials oxidation during the experiment. To study the precipitation sequence in the alloy, the shocked and un-shocked samples were subjected to a heating rate of 10\(^\circ\)C/min up to a temperature of 550\(^\circ\)C. This procedure was repeated for several samples and a good reproducibility in the plotted DSC curves was observed. To characterize the microstructural evolution during the DSC tests, samples for TEM analyses were prepared by heating in the DSC machine with the same heating profile used during the DSC experiments. Samples were removed from the DSC
apparatus and immediately quenched in cold water subsequent to achieving the temperature at which each peak in the DSC curves was observed.

To study the precipitate evolution during isothermal aging, the shocked samples were grinded on both surfaces to a total thickness of 0.5mm and then were aged at 175°C in a salt bath furnace for various periods of time. Vickers-micro hardness and TEM studies were performed on the aged samples. Hardness measurements were conducted with a 500g load. The hardness data were determined from the average of at least four readings from each sample.

TEM specimens were prepared by twin jet electro-polishing unit in a solution of 30(vol.%) HNO$_3$ and 70 (vol.%) Methanol at -20°C±5°C and 12 VDC. TEM investigation was conducted in a Philips CM200 microscope operating at 200 keV. The selected area diffraction patterns (SADs) and dark field (DF) images were analyzed in the exact <100> zone axis orientation. Due to the strong contrast of dislocations and precipitates, it was very difficult to carefully analyze the precipitate structures (especially precipitate cross sections) in the exact <100> zone axes of Aluminum. Therefore the bright field images were obtained by tilting the sample holder less than 2° away from <100> aluminum zone axes.
Fig. B.2) DSC thermogram of the as-quenched sample taken at a heating rate of 10°C/min.

Fig. B.2 shows the DSC thermogram for the as-quenched sample, heated to 550°C at a heating rate of 10°C/min. Four exothermic and one endothermic peaks were detected in the DSC and marked along the curve in sequence. The overall shape of the DSC curve is similar to those published in the literature on similar alloys [19,20].

The clustering of Mg, Si and Mg-Si atoms and GP zone formation at the early stage of precipitation in Al-Mg-Si alloys has been studied recently and their existence has been proven by 3DAP and high resolution TEM analysis [12-13]. Due to the blocky shape of the GP zones in Al-Mg-Si alloys, streaking from GP zones would not be expected to occur in diffraction pattern analyses. In addition, the atomic scattering factors
of these three elements are very close to each other. Therefore it is difficult to resolve these zones by conventional TEM imaging. Thus, the exothermic peak I can be due to the formation of clusters/GP zones during heating of the as-quenched samples. Furthermore the temperature range for the formation of GP zones is consistent with previous studies on alloys with similar chemical composition [13, 19, 20]. For example, Miao and Laughlin [19] reported the temperature range of 60-120°C for the formation of clusters/GP zones in AA6022. Therefore as for previous reports, peak I is presumed to be due to formation of atomic clusters and GP zones.

Fig. B.3) Microstructure of specimen heated up to 230°C. (a) The needle shaped β” precipitates+ Lath shaped precipitates. (b) The <100>Al SAD pattern of microstructure in (a).

The TEM micrographs corresponding to the samples heated just above peaks II, III and IV in Fig B.2 are shown in Figs. B.3, B.4 and B.5 respectively. Fig. B.3 shows the bright field (BF) TEM micrograph and selected area diffraction (SAD) pattern of the alloy heated to 230°C (peak II). The needle-shaped precipitates are distributed
homogenously in the matrix with their long axis parallel to $[100]_{\text{Al}}$ and the dark spots are needles pointing in the viewing direction (Fig. B.3a). The SAD pattern shows faint streaks along $[010]_{\text{Al}}$ and $[001]_{\text{Al}}$ due to needle-like precipitates (Fig. B.3b). The streaks seen in the diffraction pattern of Fig. 3b agree well with the diffraction pattern for $\beta''$ observed by Miao and Laughlin [19] and Murayama et al [21]. Close examination of the end-on precipitates shows that in addition to the $\beta''$ precipitates, small lath-shaped precipitates are also present, as shown at higher magnification in the upper part of Fig. B.3a. According to Chakrabarti and Laughlin [22] the habit plane and orientation relations of the lath-shaped precipitates at the late stage of overaging resembled that of $Q'$, while they were different for the lath precipitates at early stages, thus indicating that they were possible precursors to the $Q'$ phase.
Fig. B.4) (a) The microstructure of the sample heated to 275°C with heating rate of 10°C/min. The precipitates are either β’ or Q’ and are shown by arrows. (b) The <100> Al zone axes TEM diffraction pattern of microstructure (a) and its analyses (c).

Fig. B.4a shows the bright field TEM image of the precipitates after the occurrence of peak III. The diffraction pattern (Fig. B.4b) and its analyses [19] (Fig. B.4c), and close examination of the end-on precipitates in the bright field TEM image revealed the existence of two types of precipitates, the rectangle-shaped precipitates were present in addition to the rod-like β’ precipitates. The rectangle-shaped precipitates have an angle less than 11° with the nearest <100>\textsubscript{Al} zone axes which agrees well with characteristics of the Q’ precipitates [23]. Therefore one can conclude that that the
precipitate event corresponding to peak III on the DSC trace is the simultaneous precipitation of $\beta'$ and $Q'$.  

Fig. B.5) (a) The microstructure of the sample heated to 315°C with heating rate of 10°C/min. The EDS analysis indicates that the precipitates are (b) Si and (c) $\beta$. (d) $<100>$ Al diffraction pattern corresponds to microstructure (a). (e) Schematic of the diffraction pattern (d).

The energy dispersive spectrometry (EDS) analysis of precipitates on peak IV (Fig. B.5a) determined that they are Si and Mg$_2$Si phases (Fig. B.5b and c) which agrees...
well with results of Miao and Laughlin [24]. The diffraction pattern of the region containing Mg$_2$Si phases and its analysis [16] is shown in Fig. B.5d and e. The reflections other than those from the Al matrix can be indexed as those from β-Mg$_2$Si and the double diffractions between the precipitates and the matrix are indicated by open circles in Fig B.5d. The possible origin of other reflections seen in Fig. 5d can be attributed to Si particles. The analyses of diffraction pattern indicate that the Mg$_2$Si particles are related to the matrix by the cube-cube orientation relationship:

\[
\begin{align*}
[001]_{\beta\text{-cubes}} & \parallel [001]_{\text{Al}}, \\
[100]_{\beta\text{-cubes}} & \parallel [100]_{\text{Al}}, \\
[010]_{\beta\text{-cubes}} & \parallel [010]_{\text{Al}}
\end{align*}
\]

Ohmori et al. [16] and Westengen and Ryum [25] have also reported the formation of such cuboid precipitates in Al-Mg-Si alloys. Therefore the precipitate event corresponding to peak IV is due to β-cubes and Si precipitates. The broad endothermic peak V is caused by the dissolution of β-cubes and Si precipitates.
Fig. B.6) DSC curves at a heating rate of 10°C/min for samples (a) as-quenched condition (b) shock-loaded prior to DSC run.

In Fig. B.6 the DSC plots for the as-quenched and shock-loaded samples are displayed. As can be seen, while the occurrence temperature of peaks I and II and peaks I’ and II’ look similar in both the shock-loaded and un-shocked samples, the temperature formation of peaks III’ and IV’ in Fig. B.6b is lower than peaks III and IV in Fig. B.6a.

To investigate the DSC results in more detail, TEM studies were performed on the samples heated to peaks I’, II’, III’ and IV’ respectively. Conventional TEM analysis on peak I’ revealed no distinct precipitates in the microstructure and thus similar to the argument given for peak I, it was assumed that the peak I corresponds to clustering/GP zone formation. The heat of reaction corresponding to peaks I and I’ looks similar which
means that shock-loading prior to dynamic heating did not affect the formation of clustering/GP zones.

Fig. B.7 corresponds to the bright field TEM micrograph and SAD pattern of the alloy heated up to 230°C (peak II’). Similar to Fig. B.3, the needle-shaped precipitates are seen in the matrix parallel to the \(<100>_{\text{Al}}\) zone axis of the matrix (Fig. B.7a). The morphology of the precipitates and the symmetrical faint streaks in the SAD pattern (Fig. B.7b) suggest that these precipitates are \(\beta''\). Close examination of the end-on precipitates shows that in addition to the needle shaped precipitates, small lath shaped precipitates are also present. Therefore peak II’ is characterized to be due to the formation of \(\beta''\) and lath-shaped precipitates. By comparing the precipitates in peaks II and II’, one can conclude that the pre-shock loading did not have any significant effect on the nature of \(\beta''\) and lath-shaped precipitates.

Fig. B.7) The microstructure of the sample shock-loaded prior to DSC heating experiment after the occurrence of peak II’ (a) Bright field imaging (b) SAD pattern at \(<100>_{\text{Al}}\) zone axes.
Fig. B.8 shows the bright field TEM image and SAD pattern of the precipitates after the occurrence of peak III’. Although it seemed that rod-like or needle-like precipitates with different diameters were observed along [010]_{Al} and [001]_{Al} directions, close examination of the end-on precipitates revealed that most of them were rectangle-shaped. This can be seen clearly in the TEM dark field image of this sample (Fig. B.9). Diffraction pattern and analyses of the end-on precipitates in the dark field TEM image, suggests that the rectangle-shaped precipitates are Q’. It is interesting to note that while the peak III in the un-shocked sample corresponds to β’ and Q’, the exothermic peak III’ is due to the formation of Q’ precipitates. In a previous study [26], we observed similar behavior of the pre-deformed samples. This also agrees well with high resolution TEM analyses of Matsuda et al. [27]. His studies showed that Type-C precipitates (similar to Q’ phase) were typical in the deformed Al-Mg-Si alloys containing excess Si. Therefore the precipitation event corresponding to peak III’ on the DSC trace of Fig. B.6b can be characterized to be due to the precipitation of Q’.

The bright field image, the SAD pattern and the key diagram for the microstructure corresponding to the sample heated to 330°C (peak IV’) are shown in Fig. B.10a, b and c. The presence of Q’ phase can be recognized in the bright field image shown in Fig B.10a. The diffraction pattern (Fig. B.10b) and its analysis (Fig. B.10c) indicate that, similar to the un-shocked samples, the β-cubes are present and related to the matrix by the orientation relationship:
Fig. B.8) The microstructure of the sample shock-loaded prior to the DSC heating experiment after the occurrence of peak III’ (a) Bright field imaging (b) SAD pattern at <100>Al zone axes.

Fig. B.9) The <100>Al TEM dark field micrograph of the microstructure of shock-loaded sample after the occurrence of peak III’.

\[
[001]_\beta\text{-cubes} \parallel [001]_{\text{Al}}, \quad [100]_\beta\text{-cubes} \parallel [100]_{\text{Al}}, \quad [010]_\beta\text{-cubes} \parallel [010]_{\text{Al}}
\]

EDS analyses reveal that in addition to β particles, Si precipitates were also present in the microstructure. Therefore peak IV’ corresponds to the formation of β-cubes, Q’ and Si

144
precipitates. In contrast to peak IV in the un-shocked sample, the Q′ phases are present in this precipitation event, and also the peak temperature in the shock-loaded sample is shifted to lower temperature by ~50°C.

Fig. B.10) The microstructure of shock-loaded sample heated to peak IV’ (~330°C) (a) The dark field micrograph shows β-cubes (b) The diffraction pattern including <100>β-cubes and <100>Al (c) The schematic representation of (b).
The age-hardening behavior of the shock-loaded AA6022 samples was also studied. Fig. B.11 shows the hardness as a function of artificial aging time for samples with and without shock-loading at a temperature of 175°C. At the early stage of aging the hardness of the shock loaded sample is significantly higher than the un-shocked sample due to high dislocation density and other microstructural defects produced after shock-loading (Fig. B.12).

![Graph showing hardness vs. time for shock-loaded and un-shocked samples](image)

Fig. B.11) Dependence of hardness on artificial aging time at 175°C. (a) without shock-loading (b) with shock-loading.

At later stages of aging the hardness of both the shocked and un-shocked samples becomes closer and eventually both samples reach the same hardness value after 400 minutes aging at 175°C (peak of hardness). For further details, TEM analyses were performed on both samples at the peak of hardness and the results are shown in Fig. B.13.
According to the diffraction pattern and close examination of the end-on precipitates, precipitates in both samples were characterized as needle-like, $\beta''$, and lath-shaped precipitates as majority and minority phases, respectively. Note that $\beta''$ precipitates are the major precipitates responsible for the observed maximum hardness in both shocked and un-shocked samples. This agrees well with other studies on aging behavior of Al-Mg-Si alloys which show that $\beta''$ precipitates are major precipitates associated with the peak of aging [19,27,28]. Therefore one may conclude that pre-shock loading treatment did not have any significant effect on the peak of hardness and associated precipitates.

Fig. B.12) The microstructure of AA6022 after being quenched from solutionizing temperature and subsequently shock-loaded to 23 GPa.
Fig. B.13) Bright field imaging and SAD pattern at <100>Al zone axes of the microstructure of the AA6022 aged at 175°C for 500min (a-b) without shock (c-d) with shock.

The effect of shock-loading becomes more pronounced in the overaged condition. According to Fig. B.11, in the overaged condition, the hardness in the shock loaded sample decreases faster in comparison to the un-shocked material. This behavior is consistent with the DSC results of shock-loaded material (given in Fig B.6b) where the acceleration of peaks III' and IV' was observed. The DSC results and isothermal aging behavior of pre-shock loaded samples suggest that shock-loading more likely affects the phases closer to the equilibrium state (i.e. β', Q' and β phases rather than the clusters/GP
zones and $\beta''$ precipitates). As can be seen, the precipitation of $\beta''$ happens immediately after the formation of GP zones which suggests that $\beta''$ nucleates on GP zones. More detailed analyses performed by Murayama and Hono [12] confirm that GP zones provide heterogeneous nucleation sites for the $\beta''$ precipitates. Also the atomic probe field ion microscopy (APFIM) studies of Edwards et al. [13] on Al-Mg-Si alloys show that the distribution of intermediate phases strongly depends upon the distribution of co-clusters. Therefore, one can conclude that the precipitation of $\beta''$ more likely depends on clustering/GP zones rather than other microstructural defects. According to the DSC results, shock-loading did not have any significant influence on the formation of clusters/GP zones (see peak I and I’ in Fig. B.6). Therefore, it is reasonably expected that the precipitation reaction corresponding to $\beta''$ would not change either. That is why in both the shocked and un-shocked samples the exothermic peak due to $\beta''$ precipitation was at a similar position (see peaks II and II’ in Fig. B.6). However after the $\beta''$ precipitates form, the formation rate of the subsequent phases can be affected by the presence of these microstructural defects produced due to the shock process. The reason can be explained by the fact that $\beta'$ and $Q'$ form due to the growth of $\beta''$ precipitates [15, 24]. The presence of a large density of dislocations and other microstructural defects accelerates the growth rate of $\beta''$. These defects may act as rapid diffusion paths for transferring the solute atoms from the bulk to the $\beta''$ precipitates, and thus the kinetics of $\beta'$ and $Q'$ formations become faster in comparison to the un-shocked sample. It is also interesting to note that while in the un-shocked sample (Fig. B.4), both rod-like $\beta'$ and lath-like $Q'$ precipitates are present, in shock-loaded samples (Figs. B.8 and B.9) only $Q'$ precipitates are seen. The $Q'$ phase was even co-existed with equilibrium phases, $\beta$ and Si
(Fig. B.10). Therefore, one can conclude that the presence of dislocations preferentially promotes the formation of the Q' phase over the β' phase. It should be noted that both β' and Q' phases have hexagonal crystal structure, and such a promotion may not be predictable. However, it can be explained by the fact that the habit plane of Q' has been determined to be \{150\} of the aluminum matrix [23]. The repeat distance along the <150> directions of the aluminum matrix is 1.03 nm which is about the same as the lattice parameter of the Q' phase [22,23]. Therefore the precipitates tend to form as a lath so as to minimize the misfit in its surface and hence its energy. In fact, similar observations have been reported by Deschamps et al. [29] and Ringer et al. [30]. Ringer et al. [30] showed that despite similarities in the morphology and crystallography of Ω and T₁ phases, cold-working prior to aging promoted the precipitation of T₁ in an Al-Cu-Li-Mg-Ag alloy and decreased the density of Ω phases in an Al-Cu-Mg-Ag alloy.

B.5. Conclusions

The impact of shock-loading on the precipitation reaction in an Al-0.55%Mg-1.10%Si-0.06 wt% Cu was studied by means of DSC, TEM and hardness tests. The shock-loading prior to aging altered the formation temperature and the nature of the precipitation sequence in this alloy. The following conclusions were made:

1- TEM analyses on DSC peak II’ and the peak of hardness state revealed that shock-loading did not have any significant impact on the β” precipitates. This suggests that the formation of β” precipitates highly depends on the GP zones rather than other microstructural defects.
2- In the overaged condition, the shock-loaded sample showed faster hardness reduction in comparison to an un-shocked sample. TEM analyses revealed that shock-loading accelerated the rate of formation of overaged precipitates, \( Q' \) and \( \beta \).

3- TEM analyses on the DSC peaks III and III' revealed that the precipitates in the un-shocked sample were \( \beta' + Q' \), and the precipitates in the shocked sample were \( Q' \).
B.6. References


Appendix C: A novel structural-based approach to model the age hardening behavior of aluminum alloys

C.1 Introduction

We describe a new approach for modeling the age-hardening behavior of Al-Mg-Si alloys that utilizes artificial neural networks (ANN) models to connect key microstructural parameters for realistic precipitate morphologies with the age-hardening response. The aging behavior of an Al-Mg-Si alloy is modeled by a systematic combination of hardness measurements, TEM, image analysis and ANN method. The aging behavior of AA6022 during isothermal heating was characterized by hardness measurements and the structural evolution was studied by TEM. To distinguish the precipitate morphology at each stage of aging, the image analysis algorithm capable of capturing orientation gradient, nearest neighbor distances, number density, shapes, and size of precipitates was developed. A parametric study was performed to identify the significance of each precipitate parameter, and then the most important parameters were used to train the ANN model. The model combines the most important precipitate parameters including volume fraction, shape, size and distance between precipitates. It was found that the model is able to successfully predict the age hardening behavior of AA6022 in both deformed and undeformed conditions.

C.2 Background

There have been numerous research studies on aluminum alloys in recent years mainly due to the increasing demand for the utilization of lighter materials in the
automotive industry. The heat treatable 6xxx series, Al-Mg-Si alloys, are of special interest for outer panel applications, 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. However the formability and strength properties often have adverse affect on each other and thus they need to be optimized.

It is well established that the formability and strength in heat treatable aluminum alloys can be optimized by controlling the aging behavior of these alloys. Hence understanding and modeling the aging behavior of these alloys has been an area of intense activity by many researchers. In literature, one can find a range of efforts in modeling the aging behavior including atomistic modeling [1,2], process modeling [3-6] complex mathematical modeling [7], and micromechanical modeling [8]. However, most of the existing models focus on simplified situations. For instance, in the case of homogeneous precipitation, a single precipitate phase is assumed. For heterogeneous precipitation on structural defects (grain boundary, dislocations), homogeneous precipitation is assumed to be absent. In many systems, these simplifying assumptions appear somewhat unrealistic: precipitation occurs through a sequence of metastable phases, and heterogeneous and homogeneous precipitations are competing phenomena.

In view of the variety of mechanisms involved, it is hopeless to develop models for such situations at the same level of detail as the academic models. In order to understand and to model these complex situations, one has first to qualitatively characterize the relevant microstructural features and then to use them in predicting the material behavior. In this vein, application of new models capable of incorporating the most important microstructural parameters is highly desirable. The artificial neural
networks (ANN) modeling has the potential to be used for such purposes. The broad application of ANN models in materials science has been reviewed recently by Bhadeshia [9] and Raabe [10]. Particularly ANN models are useful in studying the materials behavior wherever the complexity of the problem is overwhelming from a fundamental standpoint and where simplification is unrealistic.

The present chapter is concerned with application of ANN models in predicting the aging behavior of a relatively simple system, AA6022, which is the base of a whole family of Al-Mg-Si alloys, and has been the material of choice for automotive skin panels. The aging behavior of AA6022 was studied during isothermal heating at 175°C due to its potential industrial application (Paint Bake Process). The aging behavior was characterized by hardness measurements and the structural evolution was studied by TEM. To describe the precipitate morphology at each stage of aging, the image analysis algorithm capable of characterizing orientation gradient, nearest neighbor distances, number density, shapes, and size of precipitates was developed. These features were measured after several image filtering steps to take into account only the precipitate cross sections in the image. The relation between the characterized precipitate parameters and the evolution of material hardness during aging treatment was modeled by the ANN method.

C.3 Artificial Neural Networks approach

ANN is a collection of computational cells (neurons) attached to each other through different links with adjusted weights. A forward-pass-type network consists of a number of layers with several cells. Each neuron is usually connected with all neurons in
both the previous and the next layers. The first and last layers consist of the input and output neurons. ANN learning and training is done by tuning the link strengths (weights) between the optimization variables. ANN is an effective tool when relationships and approximation of variables are needed from a given large volume of data. Complex nonlinear relationships can be identified using different ANN structures and training methods. The structure of neural network, data representation, normalization of inputs–outputs and suitable selection of activation functions have a strong influence on the efficiency and performance of the trained neural network [11].

A neural network consists of at least three layers, i.e. input $P_i$, hidden and output $a_j$ layers; Figure C.1 shows the structure of the neural network system.

![Artificial Neural Network Architecture](image)
Backpropagation training methodology is usually used in training a neural network. The net input to unit $i$ in layer $k+1$ is

$$n_i^{k+1} = \sum_{j=1}^{k} w_{i,j} a_j^k + b_i^{k+1}$$  \hspace{1cm} (C.1)$$

The output of unit $i$ will be

$$a_i^{k+1} = f^{k+1}(n_i^{k+1})$$  \hspace{1cm} (C.2)$$

where $f$ is the activation function of neurons in the $(k+1)$th layer. The performance index, which shows all the features of this compound system, is chosen as the mean squared error

$$V = \frac{1}{2} \sum_{q=1}^{Q} (t_q - a_q^M)^T (t_q - a_q^M) = \frac{1}{2} \sum_{q=1}^{Q} e_q^T e_q$$  \hspace{1cm} (C.3)$$

In Eq. (C.3), $a_q^M$ is the output of the network corresponding to the $q$th input $p_q$ at layer $M$, $t_q$ is the target, and $e_q = (t_q - a_q^M)$ is the error term. In backpropagation learning, weight update can be achieved either after the presentation of all training data (batch training) or after each input–output pair (sequential training). The weight update for the steepest descent algorithm is

$$\Delta w_{i,j} = -\alpha \frac{\partial V}{\partial w_{i,j}}$$  \hspace{1cm} (C.4)$$

$$\Delta b_i^k = -\alpha \frac{\partial V}{\partial b_i^k}$$  \hspace{1cm} (C.5)$$

where $\alpha$ is the learning rate, which should be chosen small enough for true estimate and also at the same time large enough to accelerate convergence. Effects of changes in the net input of neuron $i$ in layer $k$ to the performance index are defined as the sensitivity:
The backpropagation algorithm performed as follows: first, inputs are fed to the network and errors are calculated; second, sensitivities are propagated from the output layer to the first layer; then, weights and biases are updated [12]. This methodology has proved to be extremely useful in modeling and classification problems where properties need to be estimated as a function of a vast array of inputs [13]. Neural network analysis has had a valuable effect on materials science; by assisting the study of phenomena which are not as yet available to physical modeling. This method is used widely in process control, process design, alloy design [9] and material characterization [14].

The topology of the neural network used in this work has two hidden layers. These are controlled to have the same number of neurons (nodes). This number typically determines the capacity of the neural network. The neural-network training algorithm includes different criteria that allow ANN size expansion by adding nodes in the hidden layers.

Training is initiated with a small number of nodes. Additional nodes are then added if the error is not reduced within a specified number of iterations. Random weights for an ANN are initially assigned. A program was written for training the type of feedforward ANN. Back-propagation method is used for determining the weight relations by minimization of the total error. Nodes in the hidden layers are simultaneously added, and the new connection weights are accomplished by keeping the old weights for a number of iterations before continued training.

Several program executions were performed in order to search out for the most suitable activation functions to minimize the MSE (mean square error) of the output. The
number of neurons and epochs used in the model are optimized based on MSE to improve the model performance. The selection of an appropriate set of training cases and procedure is very important. As in any approximation, there is not a clear method to generate a comprehensive a priori estimate of the required set of training cases before knowing the outcome and convergence of the training process. Several training strategies with different data sets have to be initially applied. The training data must contain the knowledge that describes the hardness behavior within a finite domain of input and output. This is needed to allow the trained neural network to generalize the hardness response that is implicitly included in the training data. The trained neural network is then examined, and its response is compared, often visually, with the full range of trained and untrained (verification) data.

In order to select the appropriate model parameters, different activation functions were implemented at different number of neurons and epochs. The activation (transfer) functions can be any differentiable transfer function such as linear, hyperbolic tangent sigmoid or log sigmoid. After multiple iterations to minimize the $MSE$ (Mean Square error) of the model output, $hyperbolic$ $tangent$ $sigmoid$ (Eq. C.7) and $log$ $sigmoid$ (Eq. C.8) transfer functions are applied to the hidden and the output layer respectively.

$$Tansig(n) = \frac{2}{(1 + \exp(-2*n))} - 1$$  \hspace{1cm} (C.7)

$$Logsig(n) = \frac{1}{(1 + \exp(-n))}$$  \hspace{1cm} (C.8)
C.4 Experimental Plan

Aluminum alloy 6022 was received in thin plate form with a thickness of 3.07 mm. The specimens were solution treated at 550°C for 3 hours with a programmable furnace and then water-quenched to room temperature. To study the precipitate evolution during isothermal aging, the samples were aged at 175°C in a salt bath furnace for various periods of time. Vickers micro-hardness and TEM studies were performed on the aged samples.

TEM specimens were electro-polished in a solution of 300 ml 69% nitric acid + 700 ml methanol at a temperature of -20°C ± 5°C by using a twin jet electro-polishing unit. TEM investigations were carried out in a Philips TM420 microscope operating at 120KeV. Hardness measurements were conducted with a 500g load. The hardness data were determined from the average of at least four readings from each sample.

C.5 Image Processing Analysis

The image processing procedure includes image enhancement and measurement (features) extraction. Image defects which could be caused by the digitization process or by faults in the imaging set-up are corrected using Image Enhancement techniques. After that Measurement Extraction operations are used to extract useful information from the image. In unprocessed images, the useful data often represents only a small portion of the available range of digital values. Contrast enhancement is performed to change the original values such that more of the existing range is used, thus increasing the contrast between precipitates and the backgrounds. This requires identifying lower and upper
limits from the histogram and applying a transformation to stretch this range to fill the full range.

After enhancing the image quality, spatial filtering is used to improve the appearance of an image. Spatial filters are designed to emphasize specific features in an image based on their wavelengths. A wavelength is correlated to the image texture. Coarse textured areas of an image have high wavelengths, while even areas with little variation in tone over several pixels, have low wavelengths. A general filtering method involves moving a 'window' of a few pixels in dimension over each pixel in the image, applying a mathematical computation using the pixel values under that window, and changing the central pixel with the new value. The window is shifted in both the row and column dimensions one pixel at a time and the computation is repeated until the whole image has been filtered. By changing the calculation implemented and the weightings of the individual pixels in the filter window, filters can be designed to enhance several types of features.

Wiener de-noise filter is performed to smooth and reduce the noise in the image; it estimates the local mean and variance in the region of each pixel.

\[
\mu = \frac{1}{NM} \sum_{n,n',\eta} I(n_1,n_2)
\]  

(C.9)

\[
\sigma^2 = \frac{1}{NM} \sum_{n,n',\eta} I^2(n_1,n_2) - \mu^2
\]  

(C.10)

where \(\eta\) is the N-by-M neighborhood of each pixel in the image \((I)\). To produce the filtered image \((O)\), the Wiener filter is applied for each pixel using:

\[
O(n_1,n_2) = \mu + \frac{\sigma^2 - \nu^2}{\sigma^2}(I(n_1,n_2) - \mu)
\]  

(C.11)
The average of all the local calculated variances is used to replace the unknown noise variance \( \sigma^2 [16] \).

Two-dimensional Fast Fourier Transform (FFT) is performed (Eq. C.10) to characterize the image in the frequency domain, which will help in filtering and understanding the image details.

\[
F(m, n) = \sum_{x=1}^{M} \sum_{y=1}^{N} I(x, y) e^{-\frac{2\pi mx}{M}} e^{-\frac{2\pi ny}{N}}
\]  
(C.12)

where \( 1 \leq m \leq M \) and \( 1 \leq n \leq N \), \((M, N)\) is the image \((I)\) size. After FFT Transformation, image processing can be filtered before the image transformed back to the spatial domain. A low-pass filter is designed to emphasize larger, uniform areas of similar tone and remove the smaller features in an image. High-pass filters do the opposite and are used to sharpen the appearance of fine feature in an image [17].

The aim is to extract accurate information about the precipitates features. The first step includes segmenting the image to separate the precipitates from the background by thresholding the image, which is done by setting pixels values above a certain threshold value to black, and all the others to white. Due to imaging and scanning procedure, some images have defects with different sizes. Based on the precipitates statistics, a size filter is designed to clean the image from those particles.

After precipitates detection in the microstructure and using the proper image scale; size distribution measurements are performed using pixels information. The non-uniformity of precipitates distribution in an image is quantified using distribution of nearest neighbor distances measurements (Eq. C.13). Structure may exist as clustered, random or uniformly distributed. The mean nearest neighbor distance indicates the
clustering style, for a clustered structure; the mean nearest neighbor distance is generally closer than the uniform structure. For a random structure, it forms a random distribution (Poisson, Gaussian…etc), such that the standard deviation is close to zero.

\[ N(x, y) = \min_i \left( \sqrt{(y - y_i)^2 + (x - x_i)^2} \right) \]  

(C.13)

where \((x,y)\) is the coordinates of precipitate centroid, \(i\) is an index for the surrounding precipitates.

The nearest neighbor information is used to describe the structure anisotropy. Rose figure of orientation is produced to represent the preferred direction. To characterize size gradients, the size changes in both \(x\) and \(y\) directions were observed using average pixel brightness information in the two directions [18].

**C.6 Results**

Figure C.2 shows the age-hardening behavior of the AA6022 during aging at 175°C. The age-hardening behavior of AA6022 follows the classical aging behavior of precipitation hardening alloys. At the beginning the rate of hardening is very slow due to nucleation of precipitates from supersaturated matrix. After about 40min, the rate of hardening starts to increase significantly due to the growth and change in the degree of coherency between precipitates and aluminum matrix. The hardness reached to a maximum after about 8 hours aging, and afterward over-aging started due to the formation of large particles which have no coherency with the matrix.
Fig. C.2) Variation of hardness versus time for AA6022 during aging at 175°C.

The details of precipitation sequence in AA6022 have been reported by the authors elsewhere [19]. In this paragraph a brief review of precipitate types will be given. Figure C.3 shows dark field TEM images of precipitate morphologies at four different stages of aging. Figure C.3a corresponds the morphology of the precipitates after 140min aging at 175°C. The precipitates are small needle-shaped distributed in <100>Al zone axes, and the diffraction analysis of the microstructure revealed that the precipitates are $\beta''$ [20]. Figure C.3b shows the morphology of the precipitates in the peak-aged sample. The majority of precipitates is still needle-shaped distributed in <100>Al zone axes, and the minority are lath-shaped oriented with angle less than 11° from <100> aluminum zone axes. The lath-shaped precipitates are a precursor of $Q'$ phase [21]. Figure C.3c shows the microstructure of the sample in a slightly over-aged (~730 min) condition. In addition to $Q'$ and $\beta''$ precipitates, a few large rod-like precipitates were observed in the microstructure. The elongated dimension of rod-like precipitates is about 100-200 nm which agrees well with the reported size for $\beta'$ precipitates [22]. After 5500min aging the
precipitates structure were consisted of equilibrium cuboid $\beta$ [23] phase along with $Q'$ and $\beta'$ precipitates (Fig. C.3d).

Fig. C.3) TEM dark field images of precipitates after aging at 175ºC for (a) 140min, (b) 500min, (c) 730min and (d) 5500min.

Often TEM images contain distortions and noises which need to be corrected before any further analysis. A sequence of filtering procedures discussed in Section C.5 was performed to enhance the quality of the TEM micrographs. Figure C.4 shows the morphology of precipitates after a series of filtering. As it can be seen the contrast of the image has been improved, precipitates structure are more resolved and the background noise is filtered out. Figure C.4a shows a clear filtered image at 140min aging, the noise
in figure C.4b will be filtered out using FFT pattern. The redundant particles in figure C.4c are removed using a size-based filter. The image at 5500min aging (fig. C.4d) contains a background noise which has to be cleaned out.

Fig. C.4) TEM enhanced images for (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C.

The quality of previously shown images can be further enhanced by using FFT filtering procedure discussed in Section C.5. According to this technique a frequency spectrum is correlated to the precipitates size distribution. The insets in figure C.5 show the FFT pattern of the TEM images given in figure C.3. Figure C.5 shows an example for images after cutting off the undesired noise (using a band pass filter) and converting the
image from the frequency domain to the spatial domain. The precipitates with higher brightness have higher wavelength which is represented by darker color according to the frequency spectrum.

![Filtered images](image)

Fig. C.5) FFT filtering (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C, the inset is the FFT pattern.

In the next step, image analysis was performed on the filtered TEM images to extract the precipitates information. The area fraction distribution of precipitate cross sections is represented in Figure C.6. As can be seen, up to peak of aging (Fig. C.6a and
b), the mean area of precipitates remains unchanged (~34 nm²). However, the variation of precipitate area is higher at early stages of aging which may be attributed to the simultaneous nucleation and growth of $\beta^\prime$ precipitates. As we discussed earlier, at 730 min the $\beta^\prime$ and lath-shaped precipitates start to transform to $\beta'$ and $Q'$ phases with larger dimensions. This means that slightly after peak-aged condition the mean area of precipitates should increase while the variation of precipitates area should remain unchanged. This is exactly what we can see in Fig. C.6c. In another word, our image analysis procedure is able to extract the very detail information of precipitate evolution. In the overaged condition (Fig. C.6c and d) the precipitates area increases which indicates that the growth of precipitates is dominant. After 5500 min (Fig. C.6d) due to considerable growth the mean area of precipitates is almost two times the early stages of aging.
The orientation distribution of precipitates analyzed and represented in typical rose plots (Figure C.7). It can be seen that at early stages of aging (Fig. C.7a) there is no preferred orientation among the precipitates whereas in the later stages of aging, the majority of precipitates are oriented in specific crystallographic directions (Fig. C.7b-c). This is in agreement with the precipitate evolution during aging. At early stage of aging, the precipitation of small $\beta''$ precipitates is randomly in nature, assuming their precipitation is not affected by the microstructural defects present in the bulk aluminum matrix. However, at later stages of aging the growth of $\beta''$ and its transformation to $\beta'$ and
Q' happens in preferred crystallographic orientations. Once again, it can be confirmed that the details of precipitate evolution can be extracted with the image analysis procedure applied in this work.

Fig. C.7) Rose figures for Nearest Neighborhood Direction (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C.

To extract information related to the distance between precipitates, the nearest neighborhood distance between precipitates was analyzed. Figure C.8 shows that the distribution of the nearest neighborhood distance varies at different stages of aging. The
mean and STD of the distribution were calculated to determine the nature of the distribution. It was found that the nearest neighborhood distance distributions are close to random distribution; however the degree of randomness depends on the aging time. While Fig. C.8a represents a random distribution of precipitates, the degree of randomness decreases after 500 min aging (Fig. C.8b). It can be seen that at peak-aging the precipitates have uniform distribution and the mean of nearest neighborhood distance is about 20 nm. After 730 min aging time (Fig. C.8c) the non-uniformity of distribution increases and it is maxima after 5500 min aging (Fig. C.8d). The variation of precipitate nearest neighborhood distances agrees well with the precipitate evolution during aging. At early stage of aging, the $\beta''$ precipitates forms in random manner in the bulk aluminum matrix. At later stages of aging the growth of $\beta''$ precipitates and their transformation to $\beta'$ and $Q'$ phase decrease the degree of randomness which this is more pronounced in the overaged condition.
Fig. C.8) Nearest Neighborhood Distance (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C.

Figure C.9 represents the aspect ratio (major axis to minor axis ratio) variation of precipitate cross sections during aging treatment. It can be seen that while the precipitates are more or less circular (aspect ratio \( \approx 1 \)) at early stages of aging (Fig. C.9a), the aspect ratio starts to deviates from 1 (ellipsoidal precipitates). This is in fact agrees well with previous studies [18] on the aging behavior of Al-Mg-Si alloys. At 500min aging, the peak-aged condition, the majority of precipitate are \( \beta'' \) with polyhedral cross section along with minor lath-shaped precipitates which explain the tendency of aspect ratio to be larger than 1. It is interesting to note that at 730min aging which is slightly at overaging condition, the majority of precipitates show both circular and ellipsoidal cross sections (Fig. C.9c). This behavior is also in agreement with the previous precipitate analyses in
Al-Mg-Si alloys [19]. During overaging the $\beta''$ precipitates transforms to rod-like $\beta'$ and the lath-precipitates transform to $Q'$ precipitates with rectangular-shaped cross section. The formation of rod-like precipitates explains the presence of a peak for the aspect ratio of close to 1 in Fig. C.8c. At longer time, 5500min, the precipitates close to equilibrium condition [23], $\beta$, Si and $Q$ start to form which are no longer circular in cross section (Fig. C.9d).

![Graphs showing major axis to minor axis ratio distributions](image)

Fig. C.9) Major axis to minor axis ratio (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175ºC.

**C.7 Age-Hardening Model**

In this study, a model based on the ANN approach for predicting the aging behavior of AA6022 has been proposed. In Section C.7.1, a series of experimental data was used to train the model. The mean square error (MSE) was minimized by changing
the number of neurons and epochs. Once the model was established, in Section C.7.2, a parametric study was performed to study the influence of precipitate parameters on age-hardening behavior. Then the model predictions for deformed and undeformed structures were studied in Section C.7.3.

**C.7.1 Model Training and Generalization**

The extracted precipitate information is divided into two sets as training and test sets. Neural networks are trained by using a set of precipitate characteristics obtained from TEM images discussed earlier. Then, the generalization capacity is examined by extracting the precipitate information from a new set of TEM images (test sets). The training data was not used in test data. Simulations with test data repeated many times with different weight and bias initializations.

Figure C.10 shows the hardness response of ANN model after training. As it can be seen, the model outputs are in agreement with experimental hardness measurements. It is interesting to note that, despite the hardness variation is narrow for the time interval of 100 to 1000s, the trained ANN model is still able to capture the variation of hardness.
Fig. C.10) Model output for data used in training, the inset is the error curve.

In the next step the efficiency of the model needs to be improved by minimization of MSE. This was performed by changing the number of neurons and epochs. Figures C.11 and 12 show the MSE response of the ANN model as a function of number of neurons and epochs. The MSE reaches to a minimum at 25 neurons (Fig. C.11), and thus the number of neurons in the model was set to be 25. Executing the model at different number of epochs shows a slight improvement of MSE after 300 epochs (Fig.C.12).
Fig. C.11) MSE of ANN model output versus number of neurons (50 epochs).

Fig. C.12) MSE of ANN model output versus number of epochs (25 neurons in the hidden layer).
C.7.2 Parametric analysis

After establishing the model and minimization of error, a parametric study was performed to better understand the significance of each precipitate parameter on the model response, and to eliminate the redundant parameters. Table C.1 shows the weight of each input \( w_i \) averaged after several runs of ANN program; the most efficient input has the highest weight value. Among the precipitate parameters, the number of precipitates per unit area, the area of the precipitates, nearest neighborhood distance, and major to minor axes ratio of precipitates were found to strongly affect the accuracy of the model.

Table C.1) The average influence of inputs on the model after multiple program runs.

<table>
<thead>
<tr>
<th>Model Inputs ( p_i )</th>
<th>Weights ( w_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of particles per unit Area</td>
<td>16.7</td>
</tr>
<tr>
<td>Precipitates Area distribution</td>
<td>9.4</td>
</tr>
<tr>
<td>Nearest Neighborhood distance</td>
<td>6.2</td>
</tr>
<tr>
<td>Ratios of major axis to minor axis</td>
<td>5.3</td>
</tr>
<tr>
<td>Nearest Neighborhood angle</td>
<td>1.1</td>
</tr>
<tr>
<td>Precipitates orientation</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The first three parameters represent volume fraction, size and distance between precipitates. In fact, in the literature, various models based on volume fraction [24], size [25] and distance between precipitates have been reported for age-hardening of aluminum alloys. Therefore the strong dependency of model to these parameters is not surprising and agrees well with previous works.

Among the most effective parameters given in Table C.1, the ratio of major to minor axis of precipitates or the shape of precipitate cross sections, has been ignored or less studied. According to Table C.1 this shape strongly affects the hardening behavior of
the alloy. From materials science point of view, the aspect ratio represents the precipitate types. When this ratio is close to 1, the precipitates are β″ or β′ and when this ratio is larger than 1, they are lath-shaped or Q′. Depending on whether Q-type or β-type precipitates exist, the Ø angle required for dislocation to overcome the precipitates in the {111} slip planes will be different, which directly affects the hardening behavior (Orowan mechanism). This has been schematically illustrated in Figure C.13. Although recent studies by Nie and co-workers [26,27] highlight the importance of precipitate shapes on the hardening behavior of Al-Mg-Si alloys, up to authors knowledge no reports available on modeling the hardening behavior of these alloys by simultaneous incorporating of volume fraction, size, distance and shape of precipitates.
Fig. C.13) (a) The orientation relationship of rod-like precipitates in the unit crystal of aluminum matrix. The precipitates are oriented in <100> direction of aluminum. (b) The interaction of rod-like precipitates with dislocations in \{111\} plane. (c) The orientation relationship of lath-shaped precipitates in the unit crystal of aluminum matrix. The precipitates are oriented in <100> direction of aluminum. (b) The interaction of lath-shaped precipitates with dislocations in \{111\} plane. The shadowed triangle represents the \{111\} plane.
C.7.3 Model prediction

Once the model is established, its accuracy has to be verified by comparing the model predictions versus the experimental results. The term “ANN prediction” is reserved for ANN response for cases that were not used in the pretraining stages. This is used in order to examine the ANN’s ability to associate and generalize a true physical response that has not been previously “seen.” A good prediction for these cases is the ultimate verification test for the ANN models. These tests have to be applied for (input and output) response within the domain of training. It should be expected that ANN will produce poor results for data that are outside the training domain.

Undeformed structures: The model was tested against a new set of experimental microstructure and hardness data taken after 500mins and 140mins aging. According to Table C.2, the model is able to predict the hardness with maximum 2% error. It can be concluded that the developed ANN model is able to successfully predict the hardening behavior of AA6022.

Table C.2) Model prediction for data taken at 500mins and 140mins.

<table>
<thead>
<tr>
<th>Aging time (mins)</th>
<th>Experimental Vickers hardness</th>
<th>ANN Prediction of Vickers hardness (average of multiple runs)</th>
<th>Percentage Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>67.4</td>
<td>67.6</td>
<td>0.3</td>
</tr>
<tr>
<td>140</td>
<td>62.4</td>
<td>63.7</td>
<td>2</td>
</tr>
<tr>
<td>Deformed 30%-Aged 480min</td>
<td>62.5</td>
<td>63.4</td>
<td>2</td>
</tr>
</tbody>
</table>

Deformed structures: The influence of predeformation on the nature of precipitate evolution has been studied by the authors [28, 29]. It is well established that deformation is associated with the production of large number of microstructural defects which in turn
govern the nucleation rate and growth rate of precipitates. This can result in changing the
nature of precipitation sequence and precipitate characteristics. In addition, the
interaction between dislocations and precipitates results in a complex physical problem. It
is not well clear that the hardening due to precipitates or dislocations is dominant.
Therefore in deformed structures it is very difficult to model or predict the materials behavior.

To investigate the power of the ANN model and its ability to predict the
hardening behavior of predeformed structures, selected samples were analyzed in
deformed condition. This was achieved by deforming the as-quenched samples prior to
aging treatment. Figure C.14 represented the dark field imaging of precipitates after 30%
deformation and aging at 175°C after 480mins. Interestingly the model was able to predict the hardness value in the range of experimental measurements. This means that regardless of dislocation structures, the precipitate information extracted from Fig. C.14 was sufficient to forecast the hardness. In another words, the hardening behavior of AA6022 strongly depends on precipitate characteristics and less to dislocation structure.

The excellent agreement between model predictions and experimental results confirms that ANN modeling can provides a unique opportunity for materials modelers to study the materials behavior in complex structures and to develop more realistic structural based models.
C.8 Conclusions

A model based on feed-forward neural networks in simulating hardness behavior of heat treatable 6000 series, Al-Mg-Si alloys was proposed. The data extracted from image processing of TEM images for each aging time is utilized to train the neural network model. The model captures the detail of precipitate evolution by tracking the variation in volume fraction, shape, size and distance between precipitates. It is found that the resulting model is capable of predicting hardness values of deformed and undeformed structures within the range of experimental measurements with maximum 2% error. It was concluded that hardening behavior of AA6022 strongly depends on precipitate characteristics.

Fig. C.14) TEM dark field images of precipitates in a deformed sample after aging at 175°C for 480mins.
C.9. References


