Evolution Of Lamellar Structures In Al-ag Alloys

2005

Sephalika Senapati

University of Central Florida

STARS Citation

http://stars.library.ucf.edu/etd/617

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
EVOLUTION OF LAMELLAR STRUCTURES IN AL-AG ALLOYS

by

SEPHALIKA SENAPATI
B.E. National Institute of Technologies, Rourkela, 2001

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Mechanical Materials & Aerospace Engineering
in the College of Engineering & Computer Science
at the University of Central Florida
Orlando, Florida

Fall Term
2005
ABSTRACT

In the present study, the formation and the evolution of lamellar structures in different Al-Ag alloys were investigated by transmission electron microscopy (TEM). Plates of the hexagonal $\gamma$ phase form semi-coherently on the $\{111\}$ planes of the face centered cubic lattice of the alloy after the formation of Guinier-Preston zones. Guinier-Preston zones are metastable coherent pre-precipitates which are silver rich in the aluminum-rich Al-Ag alloys. The decomposition of aluminum rich Al-Ag alloys, particularly the sequence of the later stages of precipitate formation was studied. With scanning electron microscopy and high-resolution transmission electron microscopy the development of the $\gamma$ phase was investigated.

Samples cut from different Al-Ag alloys were homogenized at temperatures between 530°C to 560°C to obtain a single phase f.c.c solid solution. The samples were then quenched to room temperature, followed by heat treatments at temperatures between 140°C and 220°C for varying lengths of times.

While Guinier-Preston zones increase in diameter with increasing aging duration, silver rich platelets of the $\gamma'$ phase form. The $\gamma'$ phase is the next metastable phase in the decomposition sequence before finally the $\gamma'$ phase transforms to the stable silver-rich phase, termed $\gamma$. For samples with silver contents above 12 at.% a parallel lamellar alignment of fine $\gamma$-plates and Al-rich matrix is found after extended heat treatments. For all alloys with Ag concentrations below 12 at.% individual $\gamma$ plates are found on all four possible (111) planes of the $\alpha$ matrix.
A method is presented to calibrate the medium-magnification high-angle annular dark-field contrast in scanning transmission electron microscopy. This calibration allows for the quantitative measurement of plate thicknesses from high-angle annular dark-field scanning transmission electron micrographs of Ag₃Al plates inclined to the electron beam. Results from these measurements are in good agreement with direct bright-field micrographs of plates viewed edge-on.
Dedicated to my loving family!
I would like to extend special thanks to Dr. Helge Heinrich, my committee chair, for his encouragement and valuable advice throughout my research. I would like to express my appreciation to my thesis committee members, Dr. Kevin Coffey and Dr. Raj Vaidyanathan, for all their assistance and cooperation. I would like to thank my officemates (Ankush, Brad) for their valuable and unyielding support throughout the completion of my thesis. I am also thankful to my friends (Travis, Narayana, Balaji) for helping me with the encapsulation and melting. I would like to thank Dr. Coffey and his student Parag for the thin film preparation and Kirk for RBS measurement to confirm thickness and calibrate ion position. I would like to thank the AMPAC Faculty (Dr. Sudipta Seal and Dr. Yong ho Sohn) and MCF staffs for providing me with all the valuable resources, without which this work would not have been possible. I would like to thank Dr. G. Kostorz and E. Fischer from ETH Zurich, Switzerland, for providing the Al-22 at.% Ag alloy.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................................ x

LIST OF TABLES .......................................................................................................................... xvi

LIST OF ACRONYMS/ABBREVIATIONS .................................................................................... xvii

CHAPTER ONE: INTRODUCTION .............................................................................................. 1

1.1 Al-Ag as a model system for decomposition ....................................................................... 1

1.2 Al-Ag Alloy .......................................................................................................................... 3

1.3. Role of precipitates in hardening ....................................................................................... 4

1.4. Nucleation, Growth and Coarsening of the precipitates .................................................. 11

1.5 The structural difference between $\gamma$ and $\gamma'$ ........................................................ 16

1.6 Lamellar Microstructures.................................................................................................... 17

1.7. Quantitative HAADF-STEM ........................................................................................... 19

CHAPTER TWO: LITERATURE REVIEW .................................................................................. 20

2.1. Guinier-Preston Zone in Al based Alloys ......................................................................... 20

2.2. Nucleation, Growth and Coarsening of precipitates in Al-Ag Alloys ............................... 22

CHAPTER THREE: METHODOLOGY .................................................................................... 25

3.1 Sample A: Al-3 at.%Ag ..................................................................................................... 25

3.2 Samples B, C and D: Al-5 at.%Ag, Al-12 at.%Ag, Al-15 at.%Ag ..................................... 25

3.3 Sample E: Al-22 at.%Ag .................................................................................................. 26

3.4 Thin Film samples: (Al-15 at.%Ag, Al-17 at.%Ag, Al-20 at.% Ag) ................................. 27

3.5. Techniques Used to Prepare the TEM sample ............................................................... 27

3.5.1. Focused Ion Beam (FIB) technique ............................................................................ 27
3.5.2. Electropolishing .......................................................................................................... 28
3.5.3. Mechanical Polishing with Allied Polisher ................................................................. 28
3.5.4. Dimple Grinding ......................................................................................................... 29
3.5.5. Ion Milling .................................................................................................................. 30
3.6. Techniques Used to Study the Microstructure ................................................................... 31
3.6.1. Transmission Electron Microscopy ............................................................................. 31
3.6.1.1 Techniques used in TEM .......................................................................................... 32
  a. Conventional Imaging ................................................................................................... 32
  b. High-Resolution Imaging ............................................................................................. 35
  c. Energy-Dispersive X-ray Spectrometry (EDS) ........................................................... 36
  d. Electron Energy-Loss Spectrometry (EELS) ................................................................ 36
  e. Selected Area Electron diffraction (SAD) .................................................................... 37
3.6.2 Scanning Transmission Electron Microscopy (STEM) ............................................... 38
  3.6.2.1. HAADF (High Angle Annular Dark field)-STEM .............................................. 38
3.6.3. Scanning Electron Microscopy (SEM) ......................................................................... 41
CHAPTER FOUR: EFFECT OF HEAT TREATMENTS IN Al-Ag ALLOYS.......................... 43
  4.1 Result and Discussion (Al-3 at.% Ag) ......................................................................... 43
  4.2. Results and discussion (Al -5 at.% Ag) ...................................................................... 46
  4.3. Results and discussion (Al-12 at.% Ag) ..................................................................... 53
  4.4. Results and discussion (Al-15 at.% Ag) ..................................................................... 59
  4.5 Results and discussion (Al-22 at.%Ag) ....................................................................... 64
  4.6. Result and discussion (Thin Film Al-Ag Alloys) .......................................................... 69
CHAPTER FIVE: THICKNESS DETERMINATION OF AG2AL PLATES ......................... 75
5.1 Theory ........................................................................................................................................ 75
5.2 Results and discussion .............................................................................................................. 79
CHAPTER VI: CONCLUSION AND FURTHER SCOPE .................................................................... 85
LIST OF REFERENCES ..................................................................................................................... 88
LIST OF FIGURES

Figure 1: The Al-Ag phase diagram showing a metastable two-phase field (dotted line) ............ 3

Figure 2. Orowan’s mechanism for the movement of dislocations ............................................. 5

Figure 3. Face-centered cubic (f.c.c) and hexagonal close-packed (h.c.p) crystal structures. Also labeled are traditional “A”, “B” and “C” (111)-stacking planes. ....................................... 6

Figure 4 Atomic distortion around a positive edge dislocation line. The line is coming out of the page, and is indicated by the symbol $\perp$. The Burgers vector $\mathbf{b}$ of the dislocation is the displacement by which the lattice is distorted in any closed circuit path about the dislocation line. In this case, the lattice is distorted by one additional lattice plane, and the Burgers vector is one lattice spacing in the slip plane................................................................. 7

Figure 5. Slip on a $\{111\}$ plane in a f.c.c crystal. One total dislocation $\mathbf{b}_{\text{total}}$ of type $\frac{1}{2}\langle110\rangle$ can split into two partial dislocations, $\mathbf{b}_1$ and $\mathbf{b}_2$, of type $\frac{1}{6}\langle112\rangle$. Site labels (A,B,C) are as in Fig.2 [22]. ............................................................................................................................... 8

Figure 6. Qualitative depiction of age-hardening in alloys [22]. As time passes, the strength of the alloy increases with the formation of new phases, $\gamma$ and $\gamma'$, until overaging occurs as one phase saturates the alloy. See e.g. Ref. [8] for similar age hardening data for Al-16 at.% Ag. .............................................................................................................. 10

Figure 7. Schematic representation of a Widmanstatten structure [20]. Short dark lines represent plate shaped precipitate particles that are aligned on specific crystallographic planes of the crystalline matrix................................................................. 12
Figure 8. Total (spherical) nucleation energy (red line) as a function of nucleus size. The interfacial contribution opposes nucleation while the volumetric driving force propels nucleation. At small sizes, the interfacial term dominates and nucleation is prevented. At larger sizes, the volumetric term dominates.

Figure 9. The effect of interface type on morphology of a growing precipitate.

Figure 10. Ray path in image mode.

Figure 11. Ray diagram for two lens system.

Figure 12. (a) Bright field mode. (b) Dark field mode.

Figure 13. Ray diagram for the Selected Area Diffraction mode (SAD).

Figure 14. Ray diagram of the scanning transmission electron microscope (STEM) conventional transmission electron microscope (CTEM).

Figure 15. Ray diagram for HAADF-STEM mode.

Figure 16. Bright field image of Al-3 at.% Ag alloy, heat treated at 140°C for 36 hours.

Figure 17. Bright field image of Al-3 at.% Ag in {111} orientation, heat treated at 180°C for 4 hours. The average thickness of Ag$_2$Al plates is 15 nm.

Figure 18. Bright field TEM image of Al-3 at.% Ag sample heat treated at 180°C for 24 hours. Plates formed in all {111} orientations. The average thickness of the plates was found out to be 18 nm.

Figure 19. Bright field TEM image of Al-5 at.% Ag sample, heat treated at 180°C for 10 minutes.

Figure 20. Overview image of Al-5 at.% Ag, heat treated at 180°C for 10 minutes. The average thickness of the γ plates was found to be 9 nm.
Figure 21. Overview image of Al-5 at.% Ag, heat treated at 180°C for 4 hours. The average thickness of the γ plates is 17 nm. ................................................................. 48

Figure 22. High resolution TEM image of Al-5 at.% Ag, heat treated at 180°C for 4 hours. .... 49

Figure 23. Bright field TEM image of Al-5 at.% Ag, heat treated at 180°C for 24 hours. The average thickness of the γ plates is 26 nm. ................................................................. 50

Figure 24. Bright field TEM image of Al-5 at.% Ag heat treated at 180°C for 96 hours. The average thickness of the γ plates is 31 nm. ................................................................. 50

Figure 25. HAADF-STEM image of overview of Al-5 at.% Ag aged for 10 mins at 200°C. The average thickness of the plates was found to be 15 nm. ................................................................. 51

Figure 26. Bright field TEM image of Al-5 at.% Ag sample heat treated at 200°C for 4 hours. The average thickness of the γ plates is 25 nm ................................................................. 51

Figure 27. Variation of the average thickness of Ag2Al precipitates in Al-5 at.% Ag. ............... 52

Figure 28. Average number γ’ particles per cubic micron as a function of time for Al-5 at.% Ag. ............................................................................................................................. 53

Figure 29. High resolution TEM image of Al-12 at.% Ag, heat treated at 180°C. .................. 54

Figure 30. Bright field TEM image of Al-12 at.% Ag, heat treated at 180°C for 4 .................. 55

Figure 31. Bright field image of Al-12 at.% Ag, heat treated at 180°C for 24 ....................... 56

Figure 32. Bright field TEM image of Al-12 at.% Ag, heat treated at 200°C for ................. 57

Figure 33. Bright field TEM image of Al-12 at.% Ag, heat treated at 2000°C ...................... 58

Figure 34. Variation of average thickness of Ag2Al precipitates in Al-12 at.% Ag with aging time at 180°C ................................................................. 59

Figure 35. Bright field TEM image of Al-15 at.% Ag alloy homogenized at 550°C for 4-hours. ............................................................................................................................. 60
Figure 36. Bright field image of Al-15 at.% Ag, heat treated at 160°C for 20 hrs, showing G.P. zones. ........................................................................................................................................... 61

Figure 37. Bright field image of Al-15 at.% Ag, heat treated at 160°C for 20 hrs, showing the plates. ........................................................................................................................................... 61

Figure 38. (a) Bright field image of the Al-15 at.% Ag, showing the overview of the sample in [211] beam direction and the (b) corresponding SADP........................................................................ 63

Figure 39. The formation of Guinier-Preston zones (dark contrast) after a 4 hour heat treatment at 1400°C. ................................................................................................................................ 64

Figure 40. Bright field TEM image of Al-22 at.% Ag, showing the GP zones after a 25 hour heat treatment at 140°C................................................................................................................. 65

Figure 41. Bright field TEM image of Al-22 at.% Ag showing the Guinier-Preston after a 50 hour heat treatment at 1400°C............................................................ 65

Figure 42. Bright field image of Al-22 at.% Ag, heat treated at 140°C for 70 hours. .................... 66

Figure 43. Bright field TEM image of Al-22 at.% Ag heat treated for 91 hours at 140°C........... 66

Figure 44. Bright-field TEM image of the lamellar microstructure in a Al-22 at.% Ag sample heat-treated for 91 h at 140°C. In some areas a change of the lamellar sequence can be observed. The avg. thickness of the plate is approximately 20nm. ............................. 67

Figure 45. Bright field TEM image of Al-22 at.% Ag, heat treated for 165 mins........................ 68

Figure 46. HAADF-STEM image of the Al-15 at.% Ag alloy, heat treated at 140°C for 6 hrs. The thickness of Al-Ag layer is approximately 250 nm. ............................................................. 69

Figure 47. HAADF-STEM image of Al-17Ag on Si heat treated at 140°C for 6 hours. The thickness of the Al-Ag layer is nearly 700 nm. ................................................................. 70

Figure 48. Homogenized sample of Al-20 at.% Ag alloy. The thickness of the Al-Ag ............... 71
Figure 49. HAADF-STEM image of Al-20 at.% Ag, heat treated at 140°C for 6 hours............ 71

Figure 50. Bright field image of Al-20 at.%Ag, heat treated for 120 hrs at 160°C. Lamellar structure of Al and Ag. The average γ plate thickness is 24 nm. ................................................. 72

Figure 51. Profile from Rutherford Back Scattering (RBS) system showing the thickness and peaks of different elements (Al, Ag, Si, O). ................................................................. 73

Figure 52. (a) Schematics of the HAADF contrast for a γ-plate viewed edge-on in a wedge shaped sample with the thin part at the bottom. (b) Schematics of the HAADF contrast of a γ-plate inclined to the viewing direction in a wedge shaped TEM foil. (c) Sketch of the cross section of a TEM sample with a plate of thickness $T$ in a sample of thickness $t$, where the sample is tilted by $\phi$ with respect to the incident electron beam. ............................................. 75

Figure 53. Bright-field transmission electron micrograph of a γ-plate with a thickness of 14.4 nm viewed along [112] of an Al-5 at.% Ag sample aged for 10 min. at 473 K. ......................... 76

Figure 54. HAADF micrograph of the plate shown in Fig. 1, but inclined to the beam direction [111]. The thicknesses of the different γ-plates as determined from the contrasts in this micrograph are indicated in nm. ............................................................................................................ 80

Figure 55. HAADF micrograph of the plate shown in Fig. 1 viewed edge-on along [112]. ....... 81

Figure 56. HAADF intensities as a function of sample thickness along the plate in Fig.54. The equivalent sample thickness represents three times the width of the wedge indicated in Fig. 53. The real sample thickness measured at the inclined γ-plate locally differs slightly (up to 10 %) from this equivalent thickness as determined from the lines drawn to mark the boundary of contrast in Fig.53. .............................................................................................................. 82
Figure 57. (a) HAADF micrograph of plates viewed along [111] with \(\gamma\)-plate thicknesses indicated. (b) Schematic of the contrast for two intersecting plates.
LIST OF TABLES

Table 1. Profile of the thickness and composition taken from the RBS system............................ 74
**LIST OF ACRONYMS/ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF</td>
<td>Bright Field</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>EEL</td>
<td>Electron energy loss</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Electron Diffraction X-ray Spectroscopy</td>
</tr>
<tr>
<td>f.c.c</td>
<td>face centered cubic</td>
</tr>
<tr>
<td>GP zone</td>
<td>Guinier-Preston zone</td>
</tr>
<tr>
<td>h.c.p</td>
<td>hexagonal close packed</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>at.</td>
<td>Atomic</td>
</tr>
<tr>
<td>wt.</td>
<td>Weight</td>
</tr>
</tbody>
</table>
CHAPTER ONE: INTRODUCTION

1.1 Al-Ag as a model system for decomposition

Nanostructured metallic surfaces produced by decomposition heat treatments may provide an easier and less expensive procedure than current sequential lithographic techniques for preparing surfaces with ordered arrays of dots, disks or line. Nanostructured surfaces with parallel lines have application possibilities including diffraction gratings for high-energy ultra-violet optics, for deposition of magnetic materials to form parallel nanowires for use in computing technology, and for attachment of carbon nanotubes to the surface for use as a hydrogen sensor. Isothermal heat treatments of several Al-rich Al-Ag alloys were performed for different durations. The purpose of this research effort was to study the effects of isothermal heat treatments in the two phase region of the $\alpha$-Al solid solution and the $\gamma$ Ag$_2$Al phase.

Al-rich, supersaturated $\alpha$ (f.c.c.) Al–Ag alloys can be aged in the two-phase region to produce Ag rich $\gamma$ (h.c.p.) precipitate plates semicoherently embedded in the $\alpha$ matrix. The precipitate–matrix orientation relationship is: (0001)$_\gamma$ // (111)$_\alpha$ and [1120]$_\gamma$ // [110]$_\alpha$, and the Al–Ag phase diagram shows a single-phase region between 61 at.% Ag and 76 at.% Ag. This alloy system serves as a model system to explore precipitate growth for several reasons. First, the $\alpha$ (f.c.c.$\rightarrow$ $\gamma$ (h.c.p.) transformation is a model plane-strain transformation with relatively simple crystallography [1-3]. Second, the growth mechanisms of these precipitates have been thoroughly investigated using static and in-situ high-resolution transmission electron microscopy (HRTEM) and are understood at the atomic level for all of the precipitate interfaces [4-7]. Third,
the large difference in atomic number between Ag and Al, i.e., 47 vs. 13, yields strong compositional contrast in electron microscopy, which can be helpful when characterizing the precipitates.

The first platelet of the $\gamma'$ phase, the precursor of the Ag$_2$Al $\gamma$-phase has been investigated by several authors [8-13]. For alloys up to 25 at.% silver, a single-phase f.c.c. material can be obtained by homogenization treatments within the solid solution. Even fast quenching from the solid solution causes the formation of Ag-rich clusters 1 to 2 nm in diameter [14] being coherently embedded in the Al-rich f.c.c. matrix. Heat treatments below 250°C lead to the formation of Guinier-Preston (GP) zones, Ag-rich metastable precipitates with f.c.c. structure. These GP zones are coherently embedded in the Al-rich matrix without any misfit dislocations. Small GP zones have an irregular shape with no well-defined interfaces to the Al-rich f.c.c. matrix [14,15], while for later stages of decomposition a faceting of larger GP zones is reported [16]. For later stages plates of the $\gamma'$-phase form at the expense of the metastable GP zones which gradually dissolve in the vicinity of the $\gamma'$-plates. The $\gamma'$-plates with hexagonal structure have a composition of Ag-40 at.% Al at the boundary of the $\gamma$ single-phase region as confirmed in the present study by analysis of the diffuse electron scattering signal in the (0001) reciprocal plane. The diffuse $2k_F$ maxima ($k_F$ is the magnitude of the Fermi wave number) in reciprocal space are consistent with an aluminum content of 60 at.% [17,18].
1.2 Al-Ag Alloy

Fig.1 shows the phase diagram of Al-Ag. Alloys are defined as mixtures of metals in which at least one impurity atomic species has been added to form a solid solution and/or new ordered phases within the new metal. (In discussing solid solutions, ‘solvent’ refers to the majority species, while ‘solute’ refers to elements present in minority concentrations).

![Al-Ag Phase Diagram](image)

Figure 1: The Al-Ag phase diagram showing a metastable two-phase field (dotted line) corresponding to the formation of GP zones [8].
While creating a homogeneous binary metallic alloy, the two elements are forced to share a common crystal lattice. Many kinetic and thermodynamic factors determine which structures will ultimately form and which specific properties of the alloy result. Silver and aluminum both have the same face centered cubic (f.c.c) crystal lattice structure. Ordered phases can be compounds of elements in some fixed proportion, or with some compositional range. Phases are defined as portions of a system having uniform physical or chemical characteristics. Properties of alloys are strongly dependent on microstructure, the proportion and composition of phases present. Sometimes ground state stable phases cannot be attained within a finite amount of time or have a large energy barrier to formation. In such cases, metastable phases, or local phase minima for which there are lower energy barriers of formation than the true ground state, can and often do occur.

1.3. Role of precipitates in hardening

Precipitation hardening is a process in an alloy caused by the precipitation of a constituent from a supersaturated solid solution. This enhances the strength and hardness of metals. There are two conditions that have to be satisfied for an alloy to be age hardenable. First, the alloy is, at a specific temperature, in a state of solid solution, and at another temperature in a two-phase region. In other words the solid solubility must be higher at high temperatures than at low temperatures. Secondly, the phase that precipitates must be a coherent or semi-coherent precipitate difficult to penetrate for dislocations.
An increase in hardness is synonymous with an increased difficulty of moving dislocations. Either a dislocation must cut through the precipitate particles in its path, or it must move between them. In either case, it can be shown that a stress increase is needed to move the dislocations through a lattice containing precipitate particles. Thus, the Orowan mechanism shown in fig.(2) was proposed to explain the interaction of dislocations with precipitate particles that have grown enough for dislocation segments to be able to bend and pass between adjacent particles. It is applicable to the later stages of aging. In this mechanism the dislocation is assumed to form expanding loops around the precipitate particles [20].

![Dislocation loop left by a previous dislocation](image)

**Figure 2. Orowan’s mechanism for the movement of dislocations**

Binary f.c.c Al-Ag continues to provide an ideal prototype for precipitation studies, mainly due to the simple plane-strain transformation and small formation energetics connecting \( \alpha \) (f.c.c) and \( \gamma \) (h.c.p) phases [22]. Also, the dissimilar atomic numbers make possible high-contrast Transmission Electron Microscopy (TEM) images.
The h.c.p structure is special in that there are a basis of two atoms associated with each bravais lattice translation. The translation vectors associated with hexagonal crystal lattices are:

\[
\begin{align*}
a &= a \frac{\sqrt{3}x + y}{2}, \\
b &= a \frac{-\sqrt{3}x + y}{2}, \\
c &= cz
\end{align*}
\]

Eq. 1

![Figure 3 Face-centered cubic (f.c.c) and hexagonal close-packed (h.c.p) crystal structures. Also labeled are traditional “A”, “B” and “C” (111)-stacking planes.](image)

Where \(x, y\) and \(z\) are Cartesian unit vectors.

Dislocations are linear defects that locally distort the lattice structure along a dislocation line, e.g. as discussed in ref [21]. The magnitude and direction of the lattice distortion are given by the Burgers vector, \(b\). The dislocations in a crystal can be linear, or form loops as in fig.4. They can also separate into two partial dislocations whose beginning and end-points terminate on the original dislocation line. The motion of these partial dislocations is a source of SF defects in metals. The Burgers vector of the partial dislocations, \(b_1\) and \(b_2\), must sum to the original Burgers vector of the total dislocation \(b_{total}\).
Figure 4 Atomic distortion around a positive edge dislocation line. The line is coming out of the page, and is indicated by the symbol $\perp$. The Burgers vector $b$ of the dislocation is the displacement by which the lattice is distorted in any closed circuit path about the dislocation line. In this case, the lattice is distorted by one additional lattice plane, and the Burgers vector is one lattice spacing in the slip plane.

The motion of dislocations is associated with plastic deformation, the permanent deformation of a material, in that whole planes of atoms are moved with respect to each other by a crystal translation, unlike in bond stretching associated with linear, elastic response. This process is known as slip, the plane along which dislocation motion occurs is known as the slip plane, and the direction along which the dislocation line moves is called the slip direction. Usually the slip direction, e.g. $\frac{1}{2} <110>$ in f.c.c, is the shortest translation vector in the close-packed direction, and the slip plane is the most close-packed plane, e.g. $\{111\}$ in f.c.c. Because the macroscopic
deformation of a material requires large numbers of dislocations to move, the restriction of
dislocation motion strengthens any metal, until the ultimate tensile strength at which point there
is an incipient, localized deformation (“necking” in gauge samples).

SF can be formed by the separation of two partial dislocations. Consider a unit edge dislocation
with Burgers vector \( \mathbf{b}_{\text{total}} = \frac{1}{2} <110> \). This shear translates an “A” position atom to the next
adjacent “A” position atom for “…ABCABC…” stacking of close-packed planes. But this
translation can be achieved by two smaller translations, \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \), in \( \frac{1}{6} <112> \) directions, as
shown in Fig. 5. The energy of formation, e.g. for one total or two partial edge dislocations in
f.c.c, disregarding the core, is given by the defect energy

\[
\begin{align*}
\text{Figure 5. Slip on a \{111\} plane in a f.c.c crystal. One total dislocation } & \mathbf{b}_{\text{total}} \text{ of type} \\
& \frac{1}{2} <110> \text{ can split into two partial dislocations, } \mathbf{b}_1 \text{ and } \mathbf{b}_2, \text{ of type } \frac{1}{6} <112>. \text{ Site labels} \\
& (A,B,C) \text{ are as in Fig.2 [22].}
\end{align*}
\]
Here $\mu_s$ is the shear modulus and $\nu$ the Poisson's ratio ($-1 \leq \nu < \frac{1}{2}$), arising from bonding in an elastically isotropic material. For an edge dislocation in f.c.c with Burgers vector $b_{total}$, Eq. 3 is proportional to $\mu a^2/2 \left( \frac{1}{4} (1 + 1 + 0) = \frac{1}{2} \right)$, whereas for partial dislocations, $b_1$ and $b_2$, Eq. 1.4 is proportional to $\mu a^2/3 \left( \frac{1}{36} (1 + 1 + 4) = \frac{1}{3} \right)$. We find that splitting $b_{total}$ into two partial dislocations, $b_1$ and $b_2$, is therefore energetically favorable by Eq. 3, consistent with the sum rule for partial dislocations, Eq. 2, as discussed e.g. in Ref. [24]. Thus the elastic energy is reduced for the formation of two separate partial dislocations, called Shockley partial dislocations for the case of $b = \frac{1}{6} <112>$ in f.c.c.

It is believed that an important factor in the interaction between precipitate particles and dislocations is the presence of stress fields surrounding precipitate particles [24]. This is especially true when the precipitate particle is coherently embedded in the matrix.

Different combinations of ageing temperatures and times give different properties. Early metallurgists found that in some dilute alloys tensile-strength or hardness improved with age at
room temperature, see Fig.6. Guinier and Preston (GP) originally characterized this effect by identifying GP-zones in Al-Cu [25,26]. GP-zones are solute-rich three-dimensional clusters, ellipsoids in Al-Cu and spheroids in Al-Ag, that strengthen alloys by providing obstacles for moving dislocations. During growth, certain particles (the larger ones) continue to grow, while others (the smaller ones), disappear. As aging progresses, the size of the average particles increases, but the number of particles decreases. Maximum hardening is associated with an optimum small particle size and a corresponding large number of particles, while overaging is associated with few relatively large particles. Later work by Nicholson and Nutting identified hexagonal $\gamma$ plate precipitates in supersaturated Al-16 at.%Ag alloys [27]. Since that time many researchers have studied $\gamma$ plate growth in Al-Ag [28-30].

![Graph showing age-hardening in alloys](image)

Figure 6. Qualitative depiction of age-hardening in alloys [22]. As time passes, the strength of the alloy increases with the formation of new phases, $\gamma$ and $\gamma'$, until overaging occurs as one phase saturates the alloy. See e.g. Ref. [8] for similar age hardening data for Al-16 at.% Ag.
1.4. Nucleation, Growth and Coarsening of the precipitates

From the microstructural point of view, the first process to accompany a phase transformation is nucleation which means formation of very small (often subnanometer) particles, or nuclei, of a new phase, which are capable of growing. A precipitate particle can be nucleated, either heterogeneously or homogeneously. Heterogeneous precipitation is largely associated with dislocations, dislocation nodes, impurity particles, grain boundaries and surfaces. Homogeneous nucleation on the other hand, involves the spontaneous formation of nuclei as a result of compositional fluctuations in the matrix that are large enough to cause a second stage particle to form in an otherwise perfect crystal. Homogeneous nucleation is usually difficult to achieve and heterogeneous nucleation is typically favored [30]. Homogeneous nucleation of Guinier-Preston zones is believed to be possible in a basically continuous crystal lattice, provided a critical vacancy concentration exists. It has also been proposed that at low temperatures (below 100°C) the critical nucleus size for a GP zone may be so small that the incubation time for a nucleus effectively vanishes [31]. This would account for the rapid growth rates of the zones at these temperatures. GP zones may also form by spinodal transformation, for which there is no barrier for nucleation [31].

In many Al alloys, precipitation hardening phenomena are made even more complicated by the fact that nucleation occurs both homogeneously and heterogeneously. Preferred locations for heterogeneous nucleation in these alloys are grain boundaries and subgrain boundaries. Since heterogeneous nucleation is easier, precipitation tends to occur more rapidly at these locations. This introduces a time lag between the aging responses in areas undergoing heterogeneous and
homogeneous nucleation, and overaging frequently occurs at the grain boundaries long before precipitation in the matrix has had a chance to develop fully. Another effect of rapid precipitation at grain boundaries is that precipitate particles may grow larger in size and, as a result, deplete the solute from the areas adjacent to the boundaries [20].

Precipitate particles are not always spherical in shape. Frequently, the precipitate has a plate-like or even needle-like form. In many cases plate or needle shaped precipitate particles grow in such a manner that they are aligned along specific crystallographic planes or direction of the matrix crystals. Intersecting geometrical patterns may result from this type of precipitate growth. Such formations are called *Widmanstatten structures* (fig 7).

![Figure 7. Schematic representation of a Widmanstatten structure [20]. Short dark lines represent plate shaped precipitate particles that are aligned on specific crystallographic planes of the crystalline matrix.](image)
If a nucleus can attain a size that exceeds the maximum, $G^*$ of the curve in Fig. 8, then it can increase its size while continuously decreasing its free energy--therefore any nucleus with size $R^*$ or larger will grow continuously.

![Figure 8](image.png)

Figure 8. Total (spherical) nucleation energy (red line) as a function of nucleus size. The interfacial contribution opposes nucleation while the volumetric driving force propels nucleation. At small sizes, the interfacial term dominates and nucleation is prevented. At larger sizes, the volumetric term dominates.

$$R^* = \frac{2\gamma^{\alpha\beta}}{\Delta G_{nuc}}$$  \hspace{1cm} \text{Eq. 4}$$

Substituting this radius into the expression for the nucleation energy gives the nucleation barrier energy.
\[
G^* = \frac{16\pi (\gamma^{\alpha\beta})^3}{3(\Delta G^\text{misc})^2}
\]

This expression illustrates that nucleation must occur at a critical size and that the energy barrier to nucleation can be reduced by a decrease in the interfacial tension or by an increase in the volumetric driving force. The time required for the phase transition to occur is related to the time required for a critical composition fluctuation to occur that will produce a critical nucleus of size \(R^*\) and that time increases exponentially with the barrier \(G^*\) \cite{32}.

In most solid-solid systems, precipitates have a specific crystallographic orientation relationships with their parent phase. The movement of such an interface is accomplished through the lateral migration of stepped terraces called ledges. The interface growth kinetics depends on the ledge nucleation kinetics, the ledge height, the volume diffusion of solute to or from the interface, and the diffusion and elastic strain fields near the ledge. Therefore, growth normal to a coherent or semi-coherent interface may be slower than growth normal to a disordered boundary. For the precipitate to grow, these interfaces must migrate and the shape that develops during the growth will be determined by the relative migration rates. As ledge mechanism favors the growth of coherent interface, deficiency or insufficient supply of ledges will cause the incoherent interfaces to advance faster than the semicoherent interface. So a nucleus with one plane of good matching will grow into a thin disc or plate as shown in figure.9.
Figure 9. The effect of interface type on morphology of a growing precipitate.

(A) Low-mobility semicoherent interfaces

(B) High-mobility incoherent interfaces

During coarsening, large precipitates grow on the expense of small precipitates in the matrix. This reduces the interfacial energy in the two-phase material [33]. The microstructure of a two-phase alloy is always unstable if the interfacial free energy is not a minimum. Therefore a high density of small precipitates will tend to coarsen into a lower density of larger particles with a smaller total interfacial area. However, such coarsening often produces an undesirable degradation of properties such as a loss of strength or the disappearance of grain boundary pinning. As with grain growth, the rate of coarsening increases with temperature and is of particular concern in the design of materials for high-temperature applications. The thickening of $\gamma'$ precipitates occurs by the lateral migration of $\frac{1}{6} <112>$ Shockley partial dislocation bounded ledges along the precipitate faces [33]. The partial dislocations on every other {111}
planes convert the stacking of the \{111\} planes from the face centered cubic (f.c.c) structure of the solid solution to the hexagonal close packed (h.c.p) structure of the $\gamma'$.

1.5 The structural difference between $\gamma$ and $\gamma'$

For Al-Ag alloys the interfacial structures and growth kinetics of $\gamma$ and $\gamma'$ in Al-Ag alloys have been widely studied [34-51]. This system serves as a model for coarsening of plate shaped precipitates. An alloy that has been homogenized in the single phase $\alpha$ region, quenched, and then aged within the metastable solvus typically exhibits the following precipitation sequence

$\alpha \rightarrow \text{GP zones} \rightarrow \gamma' \rightarrow \gamma$

(except for high temperatures in the two phase region where a direct decomposition in $\alpha + \gamma$ is expected).

The $\gamma$ phase has the same composition and hexagonal structure as $\gamma'$ but slightly different lattice parameters [52]. The major change is that the lattice spacing of the close packed planes in $\gamma$ no longer is the same as the aluminum matrix. While the broad faces of the $\gamma'$ precipitates are parallel to the \{111\} planes of the matrix and some stacking faults are present in the particles, the $\gamma$ phase lost the perfect $\{0001\}_\gamma//\{111\}_\alpha$ orientation relationship. The transformation from $\gamma'$ to $\gamma$ is accomplished by the introduction of a sufficient number of misfit dislocations of appropriate Burgers vector into the broad faces of $\gamma'$ plates [46].
1.6 Lamellar Microstructures

A lamellar arrangement of $\gamma$ plates and plates of an aluminum-rich $\alpha$ matrix in Al-Ag alloy is studied in this thesis. After homogenizing the Al-Ag alloy at temperatures around $550^0C$ and quenching in ice water, G.P.zones form. The evolution of $\gamma'$ plates and the subsequent transformation to $\gamma$ phase occurs after extended heat treatments at temperatures between $180^0C$ and $220^0C$. The plate shaped precipitates have coherent broad faces parallel to the $\{111\}$ plane of the aluminum matrix, and a hexagonal closed packed crystal structure. The lamellar structure is a result of coarsening under restraints imposed by neighboring plate-like precipitates. The alternate lamellae of $\alpha$-Al matrix and $\gamma$-$\text{Ag}_2\text{Al}$ plates form after a particular heat treatment. The lamellar structure has reduced strain energy compared to randomly oriented plates. In the often studied system of Al-$\text{Ag}_2\text{Al}$ [53,34,54,40,48,56,50,51], the two phases (alternate lamellae of Al and Ag$_2$Al) give the low energy interface between $\{111\}$ in the Al matrix and (0001) in the hexagonal precipitate. This low-misfit interface forms the habit plane of the thin plate like Widmanstatten precipitates; a shape that is qualitatively expected from the “Wulff” reference theorem for minimizing the interfacial energy giving the equilibrium shape. It is found in this research project that the interlamellar spacing $S$, the length ($L$) and thickness of the plates ($t$), increase with increase in temperature. The same results have been obtained from other alloy system [34,36,54].

There are several examples of alloys in which we can find lamellar microstructures. In Ni-In alloy, the grain boundary segregation is minimized by discontinuous precipitation reaction. It represents a solid-state reaction in which an initially homogeneous supersaturated solid solution,
$\alpha_0$, is decomposed into a two-phase lamellar microstructure, $\alpha + \beta$, in the region behind the migrating reaction front. This reaction starts preferentially at high-angle grain boundaries and can be expressed by the following reaction: $\alpha_0 \rightarrow \alpha + \beta$ where $\alpha$ is the depleted solid solution single phase of $\alpha_0$ and $\beta$ represents the precipitate phase [57,58].

The grain boundary discontinuous precipitation reaction involves two important steps, namely heterogeneous boundary precipitation and concurrent boundary migration. For a quantitative analysis of the reaction, the factors that govern the kinetics have to be determined. Many theories have been proposed to account for the growth kinetics of the discontinuous precipitation [59-68]. In order to compare the observed growth kinetics with a theoretical model, the following parameters have to be measured: growth velocity, interlamellar spacing, and concentrations across the lamellar interfaces and the amount of non-equilibrium solute retained in the $\alpha$-lamellae.

Ni-Sn alloys decomposed completely by cellular precipitation reaction into a lamellar structure consisting of alternate lamellae of the $\alpha$ and $\beta$ phases at all aging temperatures [69]. The fine lamellar structure of the primary cells decomposed into a coarse lamellar structure in two stages. In the first stage, the secondary cells with larger interlamellar spacing consume the primary cells. In the second stage, the tertiary cells with an even larger inter-lamellar spacing consume the secondary cells and the primary cells.
1.7. Quantitative HAADF-STEM

The limited range of tilt angles in a transmission electron microscope often prevents to view all plate-like precipitates edge-on, thus rendering the determination of the plate thickness by direct high-resolution imaging impossible. Therefore, a high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) method is presented here which allows for the determination of thicknesses for inclined plates.

While conventional bright-field and dark-field transmission electron microscopy (TEM) as well as high-resolution TEM are strongly affected by multiple scattering, dynamical scattering effects like bent contours can be minimized using only electrons scattered at high scattering angles. Two methods allow for a quantitative study of precipitates in a matrix with electrons scattered at high scattering angles; conical dark-field transmission electron microscopy [70] and HAADF-STEM [71-73]. A new approach to calibrate and quantify HAADF-STEM micrographs is presented here.
CHAPTER TWO: LITERATURE REVIEW

The growth behavior of Ag-rich $\gamma$ (and $\gamma'$) plate shaped precipitates from supersaturated Al–Ag alloys has been investigated by many researchers. The structure and composition of $\gamma$ (Ag$_2$Al) precipitates which form in Al-Ag alloys have been widely studied by TEM due to the distinct change in crystal structure associated with the $\alpha$(FCC)$\rightarrow$$\gamma$(HCP) transformation, as well as to the large difference in atomic number (Z) between Al and Ag, which produces a strong compositional contrast by the precipitates in conventional and high-resolution TEM (HRTEM) images.

2.1. Guinier-Preston Zone in Al based Alloys

The Guinier-Preston zones in aluminum – silver system has been studied by a number of investigators, e.g.,[74-79] since it was first recognized by Guinier [80] in 1942. These have shown that for concentration less than 20 percent Ag the base sequence of stages appears to be as follows:

Supersaturated $\alpha$ $\rightarrow$ Spherical Clusters $\rightarrow$ GP zones $\rightarrow$ $\gamma'$ $\rightarrow$ stable $\gamma$ phase and equilibrium $\alpha$.

Studies of the precipitation sequences have been made on a number of aluminum alloy systems. In the aluminum precipitation hardening alloys, the precipitate particles normally only become visible in an optical microscope when the metal is in advanced stage of overaging. For example, the GP zones of the Al-Ag system can only be directly observed in the electron microscopy,
atomic force microscopy and atomic probe field ion microscopy. When Al-Ag alloys are homogenized and then quenched, the initial precipitation of Ag-rich clusters proceeds rapidly even at room temperature and leads to the formation of G.P. zones. There have been extensive studies of the kinetics of the reaction, and the resulting structure has been investigated by several authors using X-ray scattering techniques [81,82].

Early X-ray scattering investigations [83,84] revealed “halos” around the transmitted and the diffracted beams. These were interpreted as arising from spherical zones in the alloys. TEM [85] studies confirmed that the zones are spherical. Laue-transmission work by Geisler [86,87] indicated thin precipitates parallel to {111} planes, leading to the suggestion that it probably represented the initial stage in the formation of plates of the transitional $\gamma'$ phase [88].

Konno et al. [89] investigated the structure of the Ag precipitates in aged Al-Ag alloys using atomic-resolution HAADF STEM, as well as conventional TEM. They found that the alloy annealed at 140$^\circ$C for 10 hours was dominated by irregularly shaped small Ag-rich particles of 1–2 nm. Some of them exhibit a shell structure. These particles are present even within large precipitates (10–50 nm), which are often characterized by their {100} and {110} facets. In addition, HAADF-STEM images indicated that Ag atoms tend to cluster in {111} planes, criss-crossing a colony of irregularly shaped Ag precipitates. It is also suggested that the contribution from these planar Ag clusters to the observed diffuse streaks in the <111> directions is not negligible [89].
Gragg and Cohen [90] studied the shape of GP zones in Al–Ag alloys by small-angle X-ray scattering. They found zones with facets parallel to \{111\} planes of the face-centered cubic (f.c.c) Al-rich matrix. This result has been confirmed in, e.g. small-angle X-ray scattering studies by Dubey et al. [91], combined X-ray and neutron scattering measurements by Malik et al. [92] and by direct imaging methods like conventional transmission electron microscopy (TEM) [9] and atom-probe field-ion microscopy (AP-FIM) [93]. The GP zone formation in aluminum-based alloys has been proposed, by previous investigators, to take place by spinodal decomposition [94] or by homogeneous nucleation and growth [95]. GP zones are fully coherent with their matrix phase.

In a study by Legoues et al.[96], the origin of GP zone formation was examined in the Al-Ag system where the coherent f.c.c – f.c.c. interfacial energy is very small and in the Al-Cu system where this energy is much larger. It was found that the spinodal lies high enough in temperature to make spinodal decomposition a viable mechanism of GP zone formation. It was also found that, because of very low interfacial energies, homogeneous nucleation of GP zones is so easy that it begins during quenching from the solution annealing treatment, well before the spinodal region is reached. Because of the lack of thermodynamic data, a definite conclusion as to the origin of the GP zones in Al-Cu was difficult to reach.

2.2. Nucleation, Growth and Coarsening of precipitates in Al-Ag Alloys

Cahn [97] suggested that nucleation becomes detectable when the free energy of formation of the critical nucleus, \( \Delta F^* \), is less than about 60 kT. Where k is the Boltzmann constant and T is the
temperature. Alexander et al. [16] calculated the interfacial energy of Al-Ag GP zones as a
function of boundary orientation, using the discrete lattice plane model and a modified regular
solution model which provides reasonable matching with both the higher temperature region of
the GP zone solvus and experimental thermodynamic data on f.c.c Al-Ag alloys.

The growth or dissolution of a precipitate particle involves transport of solute atoms in the
neighborhood of the particle. The rate of growth is generally regarded as controlled by diffusion
in the surrounding matrix although as a result of structural imperfections the atomic mobility
may be changed from that normally observed. It was previously observed that the thickening of
the coherent $\gamma'$ precipitate occurs by the movement of new interfacial partial dislocation across
the broad faces [98].

Hren and Thomas [99] observed that the thickening of the coherent $\gamma'$ precipitate occurred by
the movement of new interfacial partial dislocation across the broad faces. Laird and Aaronson
[58] have made a detailed study of the growth of $\gamma$ precipitate in an Al-15 wt.% Ag alloy. The
broad faces of the precipitate are not fully coherent, as $\gamma'$, but have a misfit dislocation structure
composed of complex arrays of Shockley partials.

The coarsening of $\gamma'$ precipitates in Al-Ag has been investigated vastly. These plate-shaped
precipitates have coherent broad faces, a hexagonal close packed crystal structure and develop on
{111} planes of the aluminum matrix. During growth, a dispersion of non-equilibrium plate-
shaped $\gamma'$ precipitates develops. To understand the subsequent size and shape during coarsening
of these $\gamma'$ precipitates, several microstructural parameters have been experimentally determined as a function of aging time through quantitative electron microscopy by Aikin and Plichta [33]. The difference in the migration kinetics between disordered and coherent interphase boundaries can lead to growth conditions that favor the development of plate-shaped precipitates [100,101]. Howe, Aaronson, and Gronsky [51,3,6] observed the broad faces of $\gamma'$ and noted the presence of ledges with heights of two, four, and six {111} atomic planes. The fact the ledge heights are multiples of two atomic planes supports the earlier conventions that the f.c.c $\rightarrow$ h.c.p. transformation occurs by the coordinated passage of Shockley partials.

According to numerous works on plate growth [31, 32, 42], nonequilibrium plates are believed to develop for two reasons: low ledge nucleation rates, which cause a shortage of ledges on the broad faces of the precipitates, and result in a slower thickening rate than bulk diffusion rates would predict; and more efficient transfer of solute atoms to or from the edge of the growing precipitate as the radius of the growing edge becomes smaller, which is commonly known as the “point effect of diffusion”. These two effects encourage the growth of precipitates with nonequilibrium shapes.
CHAPTER THREE: METHODOLOGY

The starting materials of the alloys were 99.9999% Al and 99.999% Ag. The alloys studied in the TEM were Al-3 at.% Ag, Al-12 at.% Ag, Al-15 at.% Ag, Al-22 at.% Ag and thin film materials (Al-15 at.% Ag, Al-17 at.% Ag, Al-20 at.% Ag) on a SiO$_2$-Si substrate. The mixture of metals was encapsulated in a quartz tube in an Ar atmosphere. The alloy was then melted in a Thermoline 4800 Furnace at a temperature well above the melting temperature of Ag at 965°C.

3.1 Sample A: Al-3 at.%Ag

Discs of the Al-3 at.% Ag alloy were obtained from the Institute of Applied Physics at ETH Zurich, Switzerland, prepared with initial 99.9999%Al and 99.999%Ag. The homogenization of the samples were done at 550°C followed by quenching in ice water. Then, heat treatments were performed for selected durations and temperatures. For transmission electron microscopy, the samples were then thinned down with the help of different techniques (Allied Polisher, Dimple grinder, Electropolisher, Ion milling).

3.2 Samples B, C and D: Al-5 at.%Ag, Al-12 at.%Ag, Al-15 at.%Ag

The alloys (Al-5 at.% Ag, Al-12 at.% Ag and Al-15 at.% Ag) were prepared with initial 99.9999%Al and 99.999%Ag. The alloys were cut into several slices with the help of Buehler Isomet Low Speed Saw. Samples of 3mm diameter were taken out from the slices with a Gatan disc cutter. Homogenization of the samples was done at 550°C for 4 hours in a Thermoline 4800 furnace. Heat treatments were done at selected temperatures between 130°C to 200°C. The same
techniques (Mechanically polishing with Allied polisher, Dimple grinder, Ion milling) of thinning were performed on these samples and studied in TEM. FIB (Focused ion beam) technique was employed for some of the bulk samples.

3.3 Sample E: Al-22 at.%Ag

The Al-22 at.% Ag alloy was obtained from the Institute of Applied Physics at ETH Zurich, Switzerland. This alloy had been prepared from silver and aluminum by arc melting to form a small ingot. The sample was cut into slices 0.3 mm in thickness using a Buehler Isomet Low Speed Saw. These pieces were homogenized in a Thermoline 4800 furnace at 560°C for two hours in an air atmosphere. Samples were quenched in ice water following this heat treatment. A second heat treatment was performed at 140°C for varying lengths of time in an Isotemp 280A vacuum oven with an air atmosphere. Two methods were used for transmission electron microscopy (TEM) sample preparation. An FEI 200 TEM focused ion beam (FIB) system was used in order to cut small samples and check the homogenization status in the transmission electron microscope and to verify results obtained by other sample preparation methods. Preparation of FIB samples was performed using the ex-situ lift out method. A more efficient method of sample preparation i.e. electropolishing, was performed using a Struers jet polishing apparatus.
3.4 Thin Film samples: (Al-15 at.%Ag, Al-17 at.%Ag, Al-20 at.% Ag)

Al and Ag thin films were co-sputtered on a thermally grown SiO$_2$ substrate using ultra high vacuum dc magnetron sputtering. The system base pressure was approximately $1 \times 10^{-8}$ Torr and the purity of the Ar process gas was maintained by a hot reactive metal getter. Process gas contamination in the deposition chamber at the typical deposition pressure of 4m Torr was confirmed to be less than 10 ppm (the instrumental sensitivity limit) by closed ion-source quadrupole mass spectrometry. Samples with homogenized and precipitation conditions were studied in transmission electron microscopy. A Focused ion beam (FIB) system was used to prepare the samples for TEM study.

3.5. Techniques Used to Prepare the TEM sample

3.5.1. Focused Ion Beam (FIB) technique

Focused ion beam (FIB) systems use a finely focused beam of gallium ions that can be operated at low beam currents for imaging or high beam currents for site specific sputtering, milling or in combination with a platinum gas, for platinum deposition. This technique is used to cut out TEM samples from the bulk sample.

In the focused ion beam system (FEI 200 TEM FIB), a highly focused ion beam is aimed at a target area on the sample. As the beam scans the surface of the sample, a highly magnified image is created, allowing the system operator to clearly view the samples microscopic features. Firstly,
platinum was deposited on the targeted area. A TEM sample was cut out on both sides of Pt. layer deposited. The sample was taken out by ex-situ lift out process.

a. Ex Situ Lift Out Process

After the sample was taken out from the FIB chamber, it was placed under a Mitutoyo VM Zoom 40 optical microscope. The specimen was removed from the bulk sample using a micromanipulator with a glass needle and placed onto a holey carbon grid.

3.5.2. Electropolishing

Some of the Al-Ag alloys were thinned in an Electropolisher. Electropolishing is an efficient method of sample preparation. It was performed using a Struers jet polishing apparatus consisting of a Struers Polipower voltage source and a Struers Tenupol 2 jet-polishing apparatus. The electrolytic solution consisted of 200ml nitric acid and 600ml methanol. At 10 volt (yielding a 4.5 mA current), and with a pump speed setting of 5, a small hole appeared after typically 30 seconds. Around this hole, a sample area is appropriately thin for TEM investigation. After electropolishing the samples were dipped in methanol to remove the remaining electrolyte.

3.5.3. Mechanical Polishing with Allied Polisher

The samples were mechanically polished with an Allied polisher to a thickness less than 100 µm. Mechanical polishing takes time less time than dimple grinding and electropolishing. That is why this technique was employed first to thin down the samples to a certain thickness which requires less time to get a electron-transparent sample in the ion mill.
3.5.4. Dimple Grinding

A *GATAN* Model 656 system dimple grinder was used to pre-prepare the TEM samples. Dimple grinding offers a fast and reliable mechanical method of pre-thinning to near electron transparency reducing ion milling times and uneven thinning. The Dimple Grinder offers a means of producing quality TEM specimens having a large central area only a few microns thick surrounded by a robust outer rim.

Dimple grinding provides an exceptionally smooth surface reducing the prospect of surface irregularities developing in the final ion beam thinning operation and as a result increasing the yield of the electron transparent area. A dual measuring system, digital micrometer and analog dial indicator, provides accurate depth and thickness control to about few 1 micron. To begin, the grinding wheel is lowered until the dial indicator shows that the wheel just touches the surface of the specimen mount and zero the digital reading. The micrometer is then adjusted to set the desired final thickness on the display. Dimple grinding starts by rotating the wheel on the sample which itself rotates on a motorized disk.

After a certain length of time, the sample was flipped to the other side so that it can be thinned down from both the sides. The sample was thinned down to a thickness of less than 30 ūm and then put into Ion milling for further thinning.
3.5.5. Ion Milling

A *Fischione* 1010 Ion mill was used to get a thin electron transparent specimen for microscopy. Ion milling is used on physical science specimens to reduce their thickness to electron transparency. An inert gas, typically argon, is ionized and then accelerated toward the specimen surface. By means of momentum transfer, the impinging ions sputter material from the specimen at a controlled rate.

After dimple grinding the samples were put in the ion mill for further thinning. The Model 1010 Ion Mill is a tabletop, PC-controlled precision milling and polishing system for creating high-quality TEM specimens with large electron transparent areas. It is fully programmable and easy to use. The Model 1010 incorporates two independently adjustable, variable energy hollow anode discharge (HAD) ion sources, liquid nitrogen specimen cooling, 0° to 45° milling angles, automatic gas control, and an oil-free vacuum system for ultra-clean specimen processing. Firstly, the milling angle was set to 25° with a voltage of 5 kV and current of 5 A. The time was set according to the thickness of the sample with the laser threshold setting of ‘5’. The milling turns off automatically as soon as the sample gets a hole on its thinner part. The sample was then ready to put in the TEM.
3.6. Techniques Used to Study the Microstructure

3.6.1. Transmission Electron Microscopy

Transmission electron microscopy (TEM) is very important in the characterization of materials. The samples, 3mm in diameter, were placed into the *FEI Tecnai F30* TEM using a *FEI* double tilt holder. Bright-field images were taken to study the general overall micro- and nanostructure of the material. Diffraction patterns with Kikuchi lines were used to orient the sample for imaging parallel to the faces of the plates.

The electron microscope is used to acquire images of the electron intensity transmitted through the sample. For example, variations in the extent of electron diffraction across a thin specimen, called “diffraction contrast,” is useful for identification of defects such as dislocations, interfaces, and second phase particles. Beyond diffraction contrast microscopy, which measures the intensity of diffracted waves, in “high-resolution” transmission electron microscopy (HRTEM or HREM) the diffracted electron waves interfere constructively or destructively with the undiffracted transmitted wave depending on defocus and phase shift of the waves in the sample. This technique of “phase-contrast imaging” is used to form images of columns of atoms. TEM is such a powerful tool for the characterization of materials that some microstructural features are defined largely in terms of their TEM images. [102]
3.6.1.1 Techniques used in TEM

a. Conventional Imaging

The principle of dark-field/bright field-imaging is represented in Fig.10 by a canonical ray diagram for conventional TEM.

![Ray path in image mode.](image)

Figure 10. Ray path in image mode.
As shown in (Fig.11), the intermediate lens is using the back focal plane of the objective lens as its front image plane. We assume the illumination system provides rays that travel straight down the microscope before hitting the specimen. In Fig.9, all transmitted and all diffracted rays leaving the specimen are combined to form an image at the viewing screen. In this imaging mode, the specimen shows little contrast. By tracing the individual rays in Fig.9, one can check that each point in the back focal plane of the objective lens contains rays from all parts of the specimen. An image can also be formed with only those rays passing through one point in the back focal plane. By positioning an “objective aperture” at a specific location in the back focal plane, an image is made with only those electrons that have been diffracted by a specific angle.

This defines two imaging modes, which are shown in Fig. 12 (a and b)

- When the aperture is positioned to pass only the transmitted electrons, a bright field image is formed.
• When the aperture is positioned to pass only some diffracted electrons, a dark field image is formed.

Figure 12. (a) Bright field mode. (b) Dark field mode.
b. High-Resolution Imaging

HRTEM image is an interference pattern between the forward – scattered and diffracted electron waves emerging from the specimens. The specimen itself is approximated as a object that provides phase shifts and to a less extent, some absorption to the electron wave front, in proportion to its scattering potential. For HRTEM to provide information on atomic arrangements in a material, computer simulations of the images are usually required. HRTEM is an information transfer process with a filtering function determining the resolution and contrast [102]. High-resolution images are best understood in terms of Fourier transforms. The notation, \( F(\rho(r)) \), is used to represent the Fourier transform of the distribution of atoms in the specimen, \( \rho(r) \):

\[
F(\rho(r)) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \rho(r)e^{-i\Delta k \cdot r} \, d^3 r.
\]

The Fourier transform is a function of \( \Delta k \), a “diffraction vector”. With dimensions of inverse length, the vector \( \Delta k \) can account for the periodicities in the specimen. An objective aperture in the back focal plane of the objective lens truncates the Fourier transform of the electron wave transmitted through the specimen. An image formed with a small range of k-vectors can include only long-range spatial features. For forming a high-resolution image, the objective aperture should be large enough to include both the transmitted beam and at least one diffracted beam. The transmitted beam is required to provide a reference phase of the electron wavefront.
High-resolution images are most useful for identifying individual defects in crystals and for studying atomic arrangements at interfaces. It is capable of determining the arrangement of atoms at solid-solid interfaces such as grain boundaries and inter-phase boundaries.

c. Energy-Dispersive X-ray Spectrometry (EDS)

An x-ray spectrum is acquired from small regions of the specimen illuminated with a focused electron beam, usually using a solid-state detector. Characteristic x-rays from the chemical elements are used to determine the concentrations of the different elements in the specimen.

d. Electron Energy-Loss Spectrometry (EELS)

The electrons impinging on the sample can lose energy by a variety of mechanisms. These losses can reveal the composition of the sample in TEM. Plasmon losses are a frequent cause of energy loss. Plasmons are collective excitations of the electron gas in the material and cause typically energy losses of the incident electrons in the 10 eV range. Therefore the energy spread of the beam must be particularly small to detect such losses. In TEM, the losses predominantly occur in the bulk of the sample, as the beam travels through the thin specimen to the EELS detector on the other side. Energy losses of the electrons are measured after the high-energy electrons have traversed the specimen.
e. Selected Area Electron diffraction (SAD)

Fig.13 shows the ray diagram for a diffraction pattern in TEM. The intermediate lens is focused on the back focal plane of the objective lens and the transmitted beam and all of the diffracted beams are imaged.

The specimen is first examined in image mode until a region of interest is found. The selected area aperture is then inserted and positioned around the feature. The microscope is then switched to diffraction mode. The SAD (Selected area Diffraction) pattern that appears on the viewing screen originates from the area selected in the image mode.

Figure 13. Ray diagram for the Selected Area Diffraction mode (SAD).
3.6.2 Scanning Transmission Electron Microscopy (STEM)

Scanning transmission electron microscopy (STEM) is used for line scans to determine variations of the chemical composition across the samples. In scanning transmission electron microscopy (STEM), a narrow focused beam of electrons is moved in a television-style raster pattern across the specimen. In synchronization with the raster scan, various data from the specimen can be acquired, such as x-rays, secondary electrons, backscattered electrons and EELS spectra. Transmitted electrons are detected with a retractable detector at the bottom of the microscope column. The STEM mode of operation is especially useful for spectroscopy work, since it permits the simultaneous acquisition of “chemical maps” and micrographs of the sample. The STEM mode of operation is different from conventional TEM mode in that the objective lens is operated in tandem with the illumination lens system to assist in the formation of a sharp focused electron beam at the specimen. An annular dark-field detector can be used in the STEM mode of operation to form high-resolution images of atom columns.

3.6.2.1. HAADF (High Angle Annular Dark field)-STEM

Atomic resolved high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) has been widely used for the analysis of crystals and their defect structures, but it is a quite new technique developed in the last decade. [103]
Figure 14. Ray diagram of the scanning transmission electron microscope (STEM) and conventional transmission electron microscope (CTEM).

Fig. 14 shows a schematic with the electrons moving downwards in STEM and upwards in CTEM. According to the reciprocity rule of optics, bright-field STEM and CTEM give rise to the same image contrast due to elastic, coherent scattering (Bragg scattering). HAADF-STEM imaging, mainly due to elastic, incoherent scattering (TDS) is completely different from CTEM imaging.
The HAADF-STEM image is called Z-contrast image because of the strong dependence of the contrast on the atomic number. HAADF STEM is an ideal technique to investigate Al-Ag alloys, since Ag in Al shows a high atomic-number contrast. Therefore, image analysis of HAADF STEM micrographs leads to a very detailed characterization of Guinier-Preston zones (GP zones) and γ phase in Al-rich Al-Ag.

Figure 15. Ray diagram for HAADF-STEM mode

A STEM image is a signal recorded on the detector as a function of the probe position. The high-angle annular detector is used to exclude Bragg scattering and eliminate the phase problem [104], so that contrast reversion of HAADF-STEM images by the change of defocus and thickness is largely suppressed. In atomically resolved HAADF-STEM, the contrast of an atomic columns is
obtained as the integrated intensity for exposure, since the atoms in the column are at different in positions at different moments so that electrons are incoherently scattered, which results in thermal diffuse scattering (TDS). This is one of the reasons why HAADF-STEM image is incoherent, and may be called ‘laterally incoherent’. Another reason of the incoherent imaging is ascribed to scanning of the convergent beam. The electrons scattered from an atomic column might be different from those scattered from different atomic columns because time is different. Therefore the columns separated laterally are imaged incoherently, that is, a STEM image is transversally incoherent by nature. Therefore, HAADF-STEM imaging is incoherent [88].

3.6.3. Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope creates magnified images by using electrons instead of light waves. It shows very detailed 3-dimensional images at much higher resolution than possible with an optical microscope. The sample is placed inside the microscope's vacuum column through an air-tight door. After the air is pumped out of the column, an electron gun [at the top] emits a beam of high-energy electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. As the electron beam hits the sample, secondary electrons are emitted from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample.
“Secondary electron” emission is especially important in scanning electron microscopy (SEM). A secondary electron is an electron that is weakly bound to the sample and is ejected with a few electron volts of energy. Since these electrons have little energy, they can traverse only short distances through a material, less than about 100Å. Secondary electrons therefore originate from the near-surface region. These detected secondary electrons are highly sensitive to surface topography, being more likely to emerge from the peaks than the valleys of the surface. Secondary electron imaging (SEI) is the central technique for SEM. The number of secondary electrons emitted per incident electron is defined as the “secondary electron yield”, and can be either less than or greater than one. For energies of the incident electrons less than 1 keV, the secondary electron yield increases with incident energy, but reaches a maximum at energies of the order of 1 keV. The yield is lower at higher energies because the incident electrons penetrate too deeply into the material, and the secondary electrons cannot escape. EDX analysis system of SEM is used to perform compositional analysis on specimens. EDX analysis is useful in identifying materials and contaminants, as well as estimating their relative concentrations on the surface of the specimen.
CHAPTER FOUR: EFFECT OF HEAT TREATMENTS IN Al-Ag ALLOYS

4.1 Result and Discussion (Al-3 at.% Ag)

After 4 hours of homogenization at 550°C and quenching in water, a homogeneous sample is confirmed. The appearance of tiny spherical dark contrasts in the BF micrograph (fig.16), suggesting the presence of Ag-rich particles in the dark region. Fig. 16 is the heat treated sample at 140°C for 36 hours which also indicates small particles embedded within the large precipitates.

Figure 16. Bright field image of Al-3 at.% Ag alloy, heat treated at 140°C for 36 hours.
Annealing for 4 hrs at $180^\circ$C produced plates of Ag$_2$Al which were not aligned parallel but instead plates are found on all {111} f.c.c planes which is clearly visible in fig.17. The average thickness of the plate was found to be 15 nm. The figure shows that the plates are intersecting with each other and inhibiting the thickness. The old plates are may be the nucleation sites for the new plates. Hexagonal faces of the $\gamma$ plates are seen in this figure. Strain field is also associated with this sample which can be seen in fig.17.

![Image](image.png)

Figure 17. Bright field image of Al-3 at.% Ag in {111} orientation, heat treated at $180^\circ$C for 4 hours. The average thickness of Ag$_2$Al plates is 15 nm.
Fig. 18 shows the bright field image of the sample, heat treated at 180° C for 24 hours in which the average thickness of the plates was found to be 18 nm. Longer heat treatment of 72 hours at 180° C increase the average thickness of γ plates to about 24 nm.

Figure 18. Bright field TEM image of Al-3 at.% Ag sample heat treated at 180° C for 24 hours. Plates formed in all {111} orientations. The average thickness of the plates was found out to be 18 nm.
The plates in Al-3 at.% Ag do not change much in length with higher heat treatment temperatures and longer duration of time. In other words, the rate of increase in thickness of the plates is not much in this alloy.

These studies did not indicate any evidence of a lamellar structure in Al-3 at.% Ag, instead, the Ag$_2$Al plates appear on all four $\{111\}$ planes. These plates are faceted.

**4.2. Results and discussion (Al -5 at.\% Ag)**

The diffraction contrast in bright-field TEM images (Fig.19 and Fig.20) is sufficient to reveal the Ag-depleted zone surrounding the $\gamma$ plates, as well as the compositional fluctuations associated within the remaining $\alpha$ matrix. The Ag-depleted zone associated with each plate is readily visible as a bright (high-intensity) area surrounding each plate. The figures (Fig.19, Fig.20) show that the GP zones are dissolving as the Ag$_2$Al plates grow.
Figure 19. Bright field TEM image of Al-5 at.% Ag sample, heat treated at 1800°C for 10 minutes.

Figure 20. Overview image of Al-5 at.% Ag, heat treated at 1800°C for 10 minutes. The average thickness of the γ plates was found to be 9 nm.
The average thickness of the $\gamma$ plates was found to be 17 nm after the alloy is heat treated at 180$^\circ$C for 4 hours (fig.21). Fig.22 shows a high-resolution TEM image of the sample, which is heat treated at 180$^\circ$ for 4 hours. It shows two Ag$_2$Al precipitates whose edges are oriented perpendicular to the electron beam. The length of the longest precipitate found is 1\(\mu\)m.

Figure 21. Overview image of Al-5 at.% Ag, heat treated at 180$^\circ$C for 4 hours. The average thickness of the $\gamma$ plates is 17 nm.
Figure 22. High resolution TEM image of Al-5 at.% Ag, heat treated at 180°C for 4 hours.
Figure 23. Bright field TEM image of Al-5 at.% Ag, heat treated at 180°C for 24 hours. The average thickness of the $\gamma$ plates is 26 nm.

Figure 24. Bright field TEM image of Al-5 at.% Ag heat treated at 180°C for 96 hours. The average thickness of the $\gamma$ plates is 31 nm.
Figure 25. HAADF-STEM image of overview of Al-5 at.% Ag aged for 10 mins at 200°C. The average thickness of the plates was found to be 15 nm.

Figure 26. Bright field TEM image of Al-5 at.% Ag sample heat treated at 200°C for 4 hours. The average thickness of the γ plates is 25 nm
Fig. 25 and fig. 26 show the images of the Ag$_2$Al plates at a heat treatment of 200$^\circ$C for 10 minutes and 4 hours respectively. Fig. 27 shows the change of thickness of Ag$_2$Al plates with time at 180$^\circ$C for an Al-5 at.% Ag alloy. The graph shows that the average thickness increases with the longer duration of heat treatments.

![Graph](image)

**Figure 27.** Variation of the average thickness of Ag$_2$Al precipitates in Al-5 at.% Ag with aging time at 180$^\circ$C.

The length of the longest precipitate after the heat treatment at 180$^\circ$C for 96 hr is approximately 1.6 µm.
Fig. 28 shows that the number of particles per unit volume \( (N_v) \), increases first when the particles start to nucleate at the early stage. After at a particular size, (the critical radius, \( R^* \)) the precipitate starts to grow. The larger precipitates grow at the expense of the smaller particles. So the value of \( N_v \) starts to decrease and the average size of the precipitate increases.

![Graph showing the average number \( \gamma' \) particles per cubic micron as a function of time for Al-5 at.% Ag.](image)

Figure 28. Average number \( \gamma' \) particles per cubic micron as a function of time for Al-5 at.% Ag.

### 4.3. Results and discussion (Al-12 at.% Ag)

Fig. 29 shows a high-resolution TEM image with dislocations on the precipitate face appearing to interact with the neighboring plate and changing its thickness. We can see in this figure that the thinner plate is getting thinner whereas the larger plate is growing at the expense of the small plate. Ledges are found at the intersection of the plates.
Figure 29. High resolution TEM image of Al-12 at.% Ag, heat treated at 180\(^\circ\)C for 4 hours. The average thickness of the Ag\(_2\)Al plate was found to be 29 nm.

Fig.30 shows the Al-12 at.% Ag, heat treated at 180\(^\circ\)C for 4 hours. The average thickness of the plates found to be 27 nm after this particular heat treatment. The growth rate in this alloy is very much higher than the other alloys.
Figure 30. Bright field TEM image of Al-12 at.% Ag, heat treated at 180°C for 4 hours.
Fig. 31 shows the Al-12 at.% Ag alloy, heat treated at 180°C for 24 hours. The average thickness of the Ag₂Al plates is 31 nm.

Figure 31. Bright field image of Al-12 at.% Ag, heat treated at 180°C for 24 hours.

Fig. 32 shows the bright field TEM image of Al-12 at.% Ag alloy, which is heat treated at 200°C for 10 mins. The average thickness of the Ag₂Al plates is 250 nm. It is difficult to say whether the small plates are originating from the larger plates or the small plates are dissolving into the larger plates as we see some small plates in between the larger ones. These plates are continuous but not exactly parallel.
Figure 32. Bright field TEM image of Al-12 at.% Ag, heat treated at 200°C for 10 mins.

Fig.33 shows the Al-12 at.% Ag alloy, heat treated at 200°C for 4 hours. The average thickness of the Ag2Al plates was found out to be 360 nm. The length of the longest plate was found to be approximately 10 µm.
Figure 33. Bright field TEM image of Al-12 at.% Ag, heat treated at 2000°C for 4 hours.

The quantitative TEM results from Al-12 at.% Ag samples aged at 180°C are shown in fig.34. Lamellar microstructured $\gamma$ plates started to form in the Al-12 at.% Ag alloy after the heat treatment at 180°C for 4 hours. The plates increased in length and thickness during the longer duration and at higher temperature heat treatment. In the present study, the highest temperature of heat treatment used was 200°C. It is expected that the thickness will definitely increase with further heat treatment at higher temperatures and for longer duration of time. Fig. 34 shows the average plate thickness versus time and again a monotonic increase with time is observed. As particles are nucleated the number of precipitates per unit volume, $N_v$, increases. During coarsening particles dissolve and thus $N_v$ will decrease.
4.4. Results and discussion (Al-15 at.% Ag)

Homogenized sample was formed after the 4 hours heat treatment at 550\(^\circ\)C. The sample for TEM study was prepared in the Focused ion beam (FIB) system. Fig.35 shows the homogenized sample in which small areas of Ga depositions were found which originate from the FIB process. Fig.35 indicates that quenching was not perfect and the contrast fluctuations initiate the formation of Ag-rich clusters and G.P. zones.
Figure 35. Bright field TEM image of Al-15 at.% Ag alloy homogenized at 550°C for 4-hours.

Figs. 36, 37, 38 show the sample, heat treated at 160°C for 20 hours. This sample was prepared by dimple grinding and ion milling. Initially, Ag₂Al plates of approximately 30 nm in thickness formed during the 20 hours heat treatment at 160°C. The plates were not found in parallel arrangement. The plates are arranged with irregular spacings and on all {111} planes. GP zones of 150 – 200 nm diameter form during this heat treatment.
Figure 36. Bright field image of Al-15 at.% Ag, heat treated at 160°C for 20 hrs, showing G.P. zones.

Figure 37. Bright field image of Al-15 at.% Ag, heat treated at 160°C for 20 hrs, showing the plates.
In figure 38(a), it can be seen that one of the plate is significantly thicker than all others. That means there is a continuous process of nucleation, growth and coarsening. The large precipitates grow at the expense of the smaller precipitates. In figure 37, an aligned parallel arrangement of Al-rich $\alpha$-matrix and Ag$_2$Al plates is shown.

Fig.36 shows the GP zone starts to coarsen. In some of the areas in this sample, as in fig.37, we can see the Ag$_2$Al plates. These plates grow at the expense of the GP zones.
Figure 38. (a) Bright field image of the Al-15 at.% Ag, showing the overview of the sample in [211] beam direction and the (b) corresponding SADP.
For precipitate plates, the edges or fast growing faces of these plates have high-energy [32] disordered structures, permitting them to grow at a rate limited only by nonstructural factors such as long range volume diffusion. Conversely, the broad faces or slow growing faces of these plates are proposed [32] to have lower energy ordered (coherent or semicoherent) structures requiring them to grow only by the formation and passage of ledges laterally across the interphase boundary.

4.5 Results and discussion (Al-22 at.%Ag)

Two hours of homogenization at 560°C yielded a homogeneous sample after quenching in water as evidenced by TEM. After annealing for 4 hours at 140°C, a dense network of Guinier – Preston zones is observed (fig.39).

Figure 39. The formation of Guinier-Preston zones (dark contrast) after a 4 hour heat treatment at 1400°C.
Figure 40. Bright field TEM image of Al-22 at.% Ag, showing the GP zones after a 25 hour heat treatment at 1400°C.

Figure 41. Bright field TEM image of Al-22 at.% Ag showing the Guinier-Preston after a 50 hour heat treatment at 1400°C.
Figure 42. Bright field image of Al-22 at.%Ag, heat treated at 140°C for 70 hours.

Figure 43. Bright field TEM image of Al-22 at.% Ag heat treated for 91 hours at 140°C.
Ag₂Al plates of approximately 6 nm in thickness formed during the 70 and 90 hour heat treatments at 140°C (fig.41,42). GP zones are dissolved and two sets of $\gamma'$ plates on two different \{111\} planes are seen after the 70 hour heat treatment at 140°C (fig.42). The plates are not arranged parallel to each other, instead, plates are found on all \{111\} f.c.c planes.

Figure 44. Bright-field TEM image of the lamellar microstructure in a Al-22 at.% Ag sample heat-treated for 91 h at 140°C. In some areas a change of the lamellar sequence can be observed. The avg. thickness of the plate is approximately 20nm.
Micron-sized domains containing parallel lamellae develop during a 165 min heat treatment at 200°C (fig.45). In some regions of this sample, larger non-lamellar structures are also observed. In some areas of the sample, plates are found to be overlapped on each other. There is still an oxidation problem occurring for electropolishing method of TEM sample preparation. This was
investigated in the Scanning Electron Microscope using energy dispersive X-ray spectroscopy (EDS).

4.6. Result and discussion (Thin Film Al-Ag Alloys)

This chapter discusses the thin-film samples (Al-15 at.% Ag, Al 17 at.% Ag, Al-20 at.% Ag deposited on a Si substrate). After homogenizing at 550°C for 3 hours, the samples were put in the FIB (Focused Ion Beam) system to get the TEM samples. The samples were then studied in TEM.

Fig.46 show the Al-15 at.% Ag thinfilm alloy deposited on SiO layer, which is heat treated at 140°C for 6 hours. The γ plates did not appear significantly in this alloy.

Figure 46. HAADF-STEM image of the Al-15 at.% Ag alloy, heat treated at 140°C for 6 hrs. The thickness of Al-Ag layer is approximately 250 nm.
Fig. 47 shows the HAADF-STEM image of the Al-17 at.% Ag thin film alloy which is heat treated at 140°C for 6 hours. The bright grains in this image are Ag and the dark grains are Al due to the density difference. The upper layer shows the platinum layer deposited in Focused ion beam (FIB) system. Middle layer shows the Al-Ag thin film. The bottom dark layer is the SiO. The Ag$_2$Al plate which formed in this alloy is not hexagonal in structure.

Figure 47. HAADF-STEM image of Al-17Ag on Si heat treated at 140°C for 6 hours.

The thickness of the Al-Ag layer is nearly 700 nm.
Figure 48. Homogenized sample of Al-20 at.% Ag alloy. The thickness of the Al-Ag layer is nearly 70 nm. SiO and Si layer thickness is nearly 105 nm.

Figure 49. HAADF-STEM image of Al-20 at.% Ag, heat treated at 140°C for 6 hours.
Figure 50. Bright field image of Al-20 at.%Ag, heat treated for 120 hrs at 160°C.

Lamellar structure of Al and Ag. The average γ plate thickness is 24 nm.
The composition and the thickness of the different layers in the samples were studied in RBS (Rutherford back scattering) system using the Romp software technique. The composition was very much accurate with the original composition taken. The fig 51 show the profile of the thickness and composition taken from the RBS system.

Figure 51. Profile from Rutherford Back Scattering (RBS) system showing the thickness and peaks of different elements (Al, Ag, Si, O).

The composition and the thickness of one of the thin film sample (Al- 15 at.% Ag) from the RBS is shown as below:
Sample: Al-15 at.% Ag

Table 1. Profile of the thickness and composition taken from the RBS system.

<table>
<thead>
<tr>
<th>Layer #</th>
<th>Thickness</th>
<th>Composition (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150.00</td>
<td>Al-Ag</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al 87.0  Ag 13.0</td>
</tr>
<tr>
<td>2</td>
<td>350.00</td>
<td>SiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 33.0  O 67.0</td>
</tr>
<tr>
<td>3</td>
<td>40000.00</td>
<td>/CM²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si 100.0</td>
</tr>
</tbody>
</table>

In a small area in the Al-20 at.% Ag thin film, we could see the lamellar microstructure of 24 nm thickness but it is not continuous.

For thin-film samples, a continuous lamellar structure is difficult to be established as grain boundaries and interfaces act as nucleation sites for the growth of the Ag₂Al plates. As Al-Ag is a low temperature material, we can not make heat treatments at high temperatures.
CHAPTER FIVE: THICKNESS DETERMINATION OF AG$_2$AL PLATES

5.1 Theory

The calibration of the HAADF signal was performed using two micrographs taken from different orientations of the same sample area. In one of the micrographs a plate has to be viewed edge-on as shown schematically in Fig. 52(a). The plate thickness can therefore be measured directly (Fig. 53) as a control of the calibration procedure. The HAADF-STEM intensities for the $\gamma$-phase and for the Al-rich matrix are determined separately, if the Ag$_2$Al plates are viewed edge-on and they fully comprise the sample thickness from the top to the bottom of the thin TEM foil.

![Schematics of HAADF contrast](image)

Figure 52. (a) Schematics of the HAADF contrast for a $\gamma$-plate viewed edge-on in a wedge shaped sample with the thin part at the bottom. (b) Schematics of the HAADF contrast of a $\gamma$-plate inclined to the viewing direction in a wedge shaped TEM foil. (c) Sketch of the cross section of a TEM sample with a plate of thickness $T$ in a sample of thickness $t$, where the sample is tilted by $\phi$ with respect to the incident electron beam.

\[
t = (H+K) \cos \phi
\]
\[
T = H \sin \phi
\]
The HAADF signals from the matrix and from the $\gamma$-phase contain contributions from the contamination layers ($I_c$) and are significantly influenced by the contrast and brightness settings of the HAADF detector, the extraction voltage, the spot size, the condensed aperture diameter and the camera length. Therefore, the HAADF-STEM calibrations and experiments are performed at fixed contrast-brightness settings yielding a constant offset $I_{bg}$ of the HAADF intensity.

Figure 53. Bright-field transmission electron micrograph of a $\gamma$-plate with a thickness of 14.4 nm viewed along [112] of an Al-5 at.% Ag sample aged for 10 min. at 473 K.
The HAADF intensities $I_M$ for the Al-matrix and $I_\gamma$ for the $\gamma$-phase depend on the projected thickness of the sample ($t_M$, $t_\gamma$) and the materials contrast ($C_M$, $C_\gamma$) measured in HAADF counts per nanometer (of the projected materials thickness).

For perfectly imaging conditions, one gets

$$I_M = I_{bg} + I_c + t_M C_M \quad 7$$

$$I_\gamma = I_{bg} + I_c + t_\gamma C_\gamma \quad 8$$

For the calibration of the sample thickness $t$, a HAADF micrograph was taken with the electron beam inclined to the $\gamma$-plate. In a wedge-shaped sample area, the projection of the $\gamma$-plate also forms a wedge-shaped area of bright contrast in the HAADF micrograph as shown schematically in Fig. 52(b). For known sample geometry, i.e., the plate normal, the overall surface normal of the crystal and the two electron beam directions being known, the sample thickness can be determined from the wedge angle.

The following assumptions are used for the calibration of the sample thickness, the scattering contrast of the two phases, and for the analysis of plate thicknesses.

a) The composition of the Al-rich matrix is constant. Variations can, however, be found for early stages of the formation of the hexagonal plates when GP zones are still present and a lower Ag content is observed in the neighborhood vicinity of the $\gamma$-plates: see, e.g., [5]. For samples with $\gamma$-plates still growing in thickness in the early stages, a HAADF
intensity reduced by less than 5% in the Al-rich matrix close to the γ-plates (less than 5 nm away) is found. In the present case, samples are studied where GP zones are completely dissolved and compositional gradients near the γ-plates have not been found.

b) The composition of all γ-plates is assumed to be constant and independent of plate thickness and orientation.

c) The contamination layers on the top and the bottom surfaces of the TEM sample are assumed to be independent of the sample thickness and the position of the electron probe on the sample. Especially, it is assumed that the thickness of these contamination layers does not change at the locations where the Ag₂Al plates reach the sample surfaces. However, scanning the small electron probe over the sample causes an increase of the contamination layer by diffusion of mobile H, C, and O atoms on the surfaces. This effect is obvious if the electron beam is stopped for several ten seconds on one position and the HAADF intensity increases locally by sometimes more than 10% of the signal from the Al matrix. Therefore, the electron beam was deflected when the sample was not scanned and HAADF micrographs were recorded with scanning times in the range of ten seconds. These short scanning times prevented any significant additional contamination by exposing each measuring position to the electron beam for durations well below 1 ms.

d) The sample thickness does not change at the intersections of the Ag₂Al γ-plates with the sample surfaces. No preferential etching of one phase by the Ar-ion beam in the ion mill was observed in the current study.

e) Orientation effects can change the intensities measured with the high-angle annular detector. To minimize this effect, the smallest available camera length (80 mm) was used.
5.2 Results and discussion

The \( \gamma \)-plates appear bright in the HAADF micrographs as they contain 60 at.\% Ag, while the matrix is depleted of silver. In Fig. 54 the \( \gamma \)-plate has a [-111] plate normal, the surface normal is only a few degrees away from the [211] orientation, and the imaging direction is along the [111] direction. The projected electron path \( H \) through a [-111] plate is 3 times the plate thickness \( T \) (see Fig. 52(c)). The sample thickness was calibrated measuring the wedge angle of the plate contrast. In the upper part of Fig.54 the sample thickness increases almost linearly as the width of the plate contrast grows with increasing distance from the sample hole at the bottom of the HAADF micrograph. For this geometry the sample thickness \( t \) is three times the width \( W \) of the plate contrast.

From Fig.55 with the plate viewed edge-on along the [112] direction, the corresponding HAADF intensities within the \( \gamma \)-plate and outside the plate can be determined along the plate same plate as shown in Fig.54. The local sample thickness and the HAADF intensities can be correlated when line profiles (Fig.56) are taken along the plate and outside the plate. The slope of the intensities as a function of sample thickness yields contrasts (in units of counts per nanometer) for the \( \gamma \)-phase and for the Al-matrix for the specific settings of the microscope.
Figure 54. HAADF micrograph of the plate shown in Fig. 1, but inclined to the beam direction [111]. The thicknesses of the different $\gamma$-plates as determined from the contrasts in this micrograph are indicated in nm.
Figure 55. HAADF micrograph of the plate shown in Fig. 1 viewed edge-on along [112].

With this calibration, the thicknesses of the inclined plates visible in Figs. 54, 55 and 57 are directly determined by measuring the increase in contrast at the edge of an inclined plate. The plate thicknesses determined by this method are indicated in these micrographs. To test the method, the plate thickness of 14.4 nm as measured directly from the micrograph in Fig. 52 is compared with the thickness obtained on the same plate shown inclined in Fig. 3. For this $\gamma$-plate the calibrated contrast in Fig. 54 yields a thickness of $(15\pm2)$ nm good agreement with the direct measurement of 14.4 nm from Fig. 53.
Figure 56. HAADF intensities as a function of sample thickness along the plate in Fig.54.

The equivalent sample thickness represents three times the width of the wedge indicated in Fig. 53. The real sample thickness measured at the inclined γ-plate locally differs slightly (up to 10 %) from this equivalent thickness as determined from the lines drawn to mark the boundary of contrast in Fig.53.

Fig.57 shows a HAADF micrograph taken along [111]. Two plates are intersecting in the thin TEM sample and the HAADF intensities of both plates are adding up where both plates are on top of each other in the [111] projection. A small stripe with lower brightness in the overlap region indicates that one of the plates is intersected by the other plate on a different  {111} plane.
While for samples with 5 at.% Ag plates occur on all four equivalent \{111\} planes the situation is different for silver concentrations at or above 12 at.%. After extended heat treatments a lamellar structure locally evolves with plates aligned parallel on one specific \{111\} plane (Fig. 57). Domains of these parallel aligned plates reach \(\mu\)m size. In the neighbouring domains parallel \(\gamma\)-plates are lying on different \{111\} planes of the Al-rich matrix. For samples with high silver contents (\(\geq\) 12 at.%) the density of hexagonal \(\gamma\)-plates is so high that elastic interaction between the plates seem to favour this parallel alignment.

Fig.57(b) is the schematic diagram of the figure 57(a), showing the plates intersecting at different positions due to which the low intensity is seen in between the plates. The intensity is higher where the plates overlap on each other.
Figure 57. (a) HAADF micrograph of plates viewed along [111] with \( \gamma \)-plate thicknesses indicated. (b) Schematic of the contrast for two intersecting plates.
CHAPTER SIX: CONCLUSION AND FURTHER SCOPES

1. Detailed studies of the growth of plate like precipitates of h.c.p $\text{Ag}_2\text{Al}$ in f.c.c Al-Ag alloys have shown that there is a diffusion controlled lengthening and thickening for a given set of precipitation conditions.

2. For low Ag concentrations $\gamma$-plates are found on all four equivalent $\{111\}$ planes, while samples at and above 12 at.% Ag show a lamellar alignment of $\gamma$-plates after extended heat treatments with domains in the $\mu$m-range of parallel $\gamma$-plates on one of the four $\{111\}$ planes of the Al-rich matrix.

3. The lamellar microstructure forms due to the coarsening of the GP zones or in other word the $\text{Ag}_2\text{Al}$ plates form at the expense of GP zones.

4. It is very difficult to get a continuous lamellar microstructure in thin film alloys as the grain boundary acts as a nucleation site for the growth of $\text{Ag}_2\text{Al}$ plates.

5. The thickness of $\text{Ag}_2\text{Al}$ $\gamma$-plates embedded semi-coherently in an Al-rich matrix can be determined from low-resolution HAADF STEM images. The HAADF signals of the Al-rich matrix and the $\text{Ag}_2\text{Al}$ phase increase linearly with increasing sample thickness up to a thickness of 200 nm. Dynamical scattering effects are therefore not significant for HAADF micrographs where atomic column resolution (see, e.g., [11,15]) is not reached.
6. This research should be extended to clarify whether lamellar structures can be reproducibly established or not.

7. The domain size (the diameter of regions with a parallel arrangement of plates) of the lamellar microstructure, observed in this study never exceeds a few micrometers. Further studies on increasing these domain sizes with parallel aligned lamellae and the ways to do this are required.

8. Oxidation is a problem when using electropolishing in this project. Further studies and research to establish a modulated surface structure can only be successful with an appropriate selection of an electrolyte for preferential etching of one phase on the surface.

9. Nanowires: Material deposition in nanogrooves has vast scopes in optics, magnetics, and computer applications. Mechanical creation of nanoscale wires may allow diffraction grating to be created for use with photon energies in the ultra violet region. Manufacturing of aligned magnetic nanowires can create novel properties that will allow further miniaturization of computer memory storage devices at an inexpensive price.

10. Carbon Nanotubes: Many useful applications may be realized if oxide-free Al-Ag nanostructured surfaces can be formed. It can be used in hydrogen gas sensor application, if carbon nanotubes could be attached to one of the phases on the surface.

11. Application of quantitative HAADF STEM on nanoparticles: If a calibration of elemental contrasts is available, they can be used to measure the thicknesses of nano or microparticles from one projected image.

12. Application of quantitative HAADF STEM for tilt series of 3D objects would provide tomographic information on their three dimensional shape and density. This is only
possible with HAADF, as there is no or only limited influence of multiple diffraction and the intensities are linearly dependent on the local thickness.
LIST OF REFERENCES


20. Trobert E. Reed-Hill, Reza Abbaschian, Physical metallurgy principles.


22. Daniel K. Finkenstadt, Mechanism for $\gamma$ precipitation in Al-Ag alloys., Dissertation at University of Illinois at Urbana-Champaign 2005


32. D. A. Porter, K. E. Easterling, Phase transformation in metals and alloys.


79. K. Hono and Hirano K-I, Early stages of decomposition of alloys (spinodal or nucleation).


