5-6-2014

Structure/Property Relationships in Two Novel Powder-Processed Al-Transition Metal-Rare Earth Alloys

Mauricio A. Gordillo
maugor@yahoo.com

Follow this and additional works at: https://opencommons.uconn.edu/dissertations

Recommended Citation
https://opencommons.uconn.edu/dissertations/391
Structure/Property Relationships in Two Novel Powder-Processed Al-Transition Metal-Rare Earth Alloys

Mauricio Andres Gordillo, PhD
University of Connecticut, 2014

Abstract
There has been significant interest in Al-rich Al-Transition Metal-Rare Earth element alloys due to the variety of metastable phases that can be formed. Here a series of microstructural studies is presented on two powder-processed alloys consolidated by warm extrusion: Al-Ni-Co-Zr-Y and Al-Mn-Ce. The microstructures of the alloys in the as-extruded condition and after heat-treatment were evaluated by X-ray diffraction and electron microscopy techniques and these correlated with the mechanical responses. For the Al-Ni-Co-Zr-Y alloy, the microstructure in all samples contains 22% by volume of Al$_{19}$(Ni,Co)$_5$Y$_3$ plates surrounded by grains of Al. The softening of the alloy is limited for heat-treatment temperatures of up to 400˚C, and the Al$_{19}$(Ni,Co)$_5$Y$_3$ plates coarsen slowly. At higher temperatures abnormal coarsening is observed with the development of a secondary population of much larger Al$_{19}$(Ni,Co)$_5$Y$_3$ plates. An analysis of the coarsening kinetics reveals that the particles coarsen by Ostwald-type ripening. There is a distinct transition in the activation energies suggesting that normal coarsening occurs at lower temperatures by short circuit diffusion, whereas abnormal coarsening develops at higher temperatures by lattice diffusion. The Al grain size is dictated by the inter-particle separation, and grain growth is limited by the extent of plate coarsening. For the Al-Mn-Ce alloy, the powder microstructure consists mainly of an amorphous phase, Al, and a
previously unreported phase, Al$_{20}$Mn$_2$Ce. The extrudate is fully devitrified and contains a mixture of Al, Al$_{20}$Mn$_2$Ce and Al$_6$Mn, with a small amount of Al$_{12}$Mn and Al$_{11}$Ce$_3$. Upon heat-treatment at up to 450°C the Al$_{20}$Mn$_2$Ce and Al$_6$Mn phases decompose to give a hard stable phase mixture with 72-73% Al$_{12}$Mn plus 13-14% each of Al$_{11}$Ce$_3$ and Al. Heat treatments at 500°C give a much softer phase mixture consisting of 60% Al, 22% of an unknown Al$_3$(Mn,Ce) phase, 9% Al$_{12}$Mn, 8% Al$_6$Mn and 1% Al$_{11}$Ce$_3$. The formation of large volume fractions of Al$_{12}$Mn for heat-treatments at up to 450°C suggests that the presence of Ce may stabilize this phase. These two systems could form the basis of new high-strength, low-density Al-based alloys with enhanced elevated temperature properties.
Structure/Property Relationships in Two Novel Powder-Processed Al-Transition Metal-Rare Earth Alloys

Mauricio Andres Gordillo

B.S., Florida Atlantic University, 2006
M.S., University of Connecticut, 2011

A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy
at the
University of Connecticut

2014
APPROVAL PAGE

Doctor of Philosophy Dissertation

Structure/Property Relationships in Two Novel Powder-Processed Al-Transition Metal-Rare Earth Alloys

Presented by

Mauricio Andres Gordillo, B.S., M.S.

Major Advisor __________________________________________________________

Dr. Mark Aindow

Associate Advisor ______________________________________________________

Dr. Harold Brody

Associate Advisor ______________________________________________________

Dr. Rainer Hebert

University of Connecticut

2014
Acknowledgments

I would like to thank my major advisor, Dr. Mark Aindow, for taking me on as one of his graduate students. I owe the successful completion of my Ph.D. dissertation to his patience, pedantry, and most importantly, to the confidence he had in me. I feel very honored to have been given the opportunity to work with Mark and will not forget everything he has taught me. I also want to give my appreciation to my associate advisors Dr. Harold D. Brody and Dr. Rainer Hebert for all of their helpful feedback and discussions. I want to acknowledge my collaborators at Pratt and Whitney and United Technologies Research Center, in particular Dr. Tom Watson for funding of the project and providing the different alloys, and Dr. Iuliana Cernatescu and Dr. T.T. Aindow for their collaboration on the Al-Mn-Ce paper.

Thanks are given to Dr. Roger Ristau and Dr. Lichun Zhang for their helpful advice and assistance with the electron microscopy facilities at IMS. I also want to thank all of my group members and all the friends I have made while at UConn for their support and encouragement, especially during those more daunting days.

I want to give special thanks to Dr. Gary Salivar at Florida Atlantic University and to Dr. Thomas O’Connell at HEICO Aerospace. I will not forget all of the helpful discussions and the encouragement to apply to graduate school. I also want to recognize Mark Johnson for being the one friend that consistently pushed me to pursue my Ph.D.

I want to thank everyone back home for their love and support throughout this experience, especially my family: Mami, Alejandro, Jessica, Jovanni, James and Wita. Finally, I want to thank Allison for sticking (very patiently) by me through the final stages of this demanding endeavor. I love you all very much.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td>viii</td>
</tr>
<tr>
<td><strong>Chapter 1: Introduction</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Advantages of Al alloys</td>
<td>3</td>
</tr>
<tr>
<td>1.1.1 Density</td>
<td>3</td>
</tr>
<tr>
<td>1.1.2 Processing</td>
<td>3</td>
</tr>
<tr>
<td>1.1.3 Oxidation Resistance</td>
<td>4</td>
</tr>
<tr>
<td>1.2 Disadvantages of Al alloys</td>
<td>4</td>
</tr>
<tr>
<td>1.2.1 Limited Strength at Room and Elevated Temperatures</td>
<td>4</td>
</tr>
<tr>
<td>1.2.2 Lack of Endurance Limit</td>
<td>5</td>
</tr>
<tr>
<td>1.3 New High Strength Al alloys</td>
<td>5</td>
</tr>
<tr>
<td>1.4 Objectives and Approach of this study</td>
<td>7</td>
</tr>
<tr>
<td>1.5 Structure of this Thesis</td>
<td>8</td>
</tr>
<tr>
<td><strong>Chapter 2: Metastable Vitreous Intermediates, Al-TM-RE Alloys</strong></td>
<td>9</td>
</tr>
<tr>
<td>2.1 General Metallic Glass Formation</td>
<td>10</td>
</tr>
<tr>
<td>2.1.1 Preparation Techniques</td>
<td>11</td>
</tr>
<tr>
<td>2.2 Amorphous Al alloys</td>
<td>12</td>
</tr>
<tr>
<td>2.3 Partially Devitrified Al Amorphous Alloys</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1 Crystallization of Amorphous alloys</td>
<td>13</td>
</tr>
<tr>
<td>2.3.2 Effects of Nano-Scale Particles on Mechanical Properties</td>
<td>15</td>
</tr>
<tr>
<td>2.3.3 Proposed Mechanisms for Improved Mechanical Properties</td>
<td>17</td>
</tr>
<tr>
<td>2.4 Fully Devitrified Amorphous Al alloys</td>
<td>18</td>
</tr>
<tr>
<td>2.4.1 Al-RE-TM Microstructures</td>
<td>19</td>
</tr>
</tbody>
</table>
5.1.4 Coarsening of the 19-5-3 Phase 51
5.1.5 Grain Growth in the FCC Al Phase 53

5.2 Discussion 55
5.2.1 Overall Microstructure and Hardness 55
5.2.2 Coarsening of the Microstructure 58

5.3 Conclusions 62

Chapter 6: Al-Mn-Ce Alloy 64

6.1 Results 65
6.1.1 Starting Microstructure 65
6.1.2 Effect of Heat-Treatment on Hardness 67
6.1.3 Development of Microstructure at 350°C 68
6.1.4 Effect of Temperature for 48h Heat-Treatments 70

6.2 Discussion 74
6.3 Conclusions 78

Chapter 7: Summary and Future Work 80

7.1 Al-Ni-Y based Alloy 81
7.2 Al-Mn-Ce based Alloy 81

References 83
Preface

The work presented in this thesis was performed at the University of Connecticut (UConn, Storrs, CT) between August 2008 and May 2014. This work was a part of the Structural Amorphous Metals (SAM) project, which was sponsored jointly by Pratt & Whitney and the Defense Advanced Research Projects Agency (DARPA). Dr. Thomas Watson at Pratt & Whitney provided the starting material for the Al-Ni-Co-Zr-Y and Al-Mn-Ce alloys and the heat-treated samples for the Al-Mn-Ce study. The XRD data presented for the Al-Mn-Ce alloy were acquired by Dr. Iuliana Cernatescu at Pratt & Whitney. Some of the TEM data for the Al-Mn-Ce alloy were acquired by Dr. T.T. Aindow at United Technologies Research Center. All of the remaining experimental work was performed using the equipment and characterization facilities at the Institute of Materials Science (IMS) at UConn. The experimental results, discussion and conclusions presented in this dissertation form the basis for two journal papers:


Chapter 1: Introduction

1.1 Advantages of Al alloys

1.1.1 Density
1.1.2 Processing
1.1.3 Oxidation Resistance

1.2 Disadvantages of Al alloys

1.2.1 Limited Strength at Room and Elevated Temperatures
1.2.2 Lack of Endurance Limit

1.3 New High Strength Al alloys

1.4 Objectives and Approach of this Study

1.5 Structure of this Thesis
Chapter 1: Introduction

One of the main concerns in modern aerospace technology is that the current levels of efficiency are not consistent with increasingly severe economic and environmental constraints. There are several ways in which this issue could be addressed, but by far the most direct is to reduce the weight of the aircraft and thereby to increase the performance. As a result, there has been a trend towards more extensive use of low density metals such as Ti, Mg, and Al, or even lighter materials such as polymers and composites. While the use of these latter non-metallic materials offers very significant potential weight savings, there are still many components for which the use of metals is essential. For example, Ti is used extensively in gas turbine engines because of its good elevated temperature strength and oxidation resistance. Mg is another low density metal that shows good strength and fatigue properties, and can be age-hardenable. Unfortunately, Ti has an extremely high production cost, and Mg can have issues relating to its corrosion and oxidation resistance, and there are some difficulties in obtaining good quality castings. Al costs much less to produce than Ti, has better oxidation and corrosion resistance than Mg, and can be processed easily by a wide variety of techniques. Unfortunately, the maximum strength of Al alloys is rather limited. As a result, there has been extensive research focused on improving the mechanical properties of Al, with the objective of expanding the range of applications for which such alloys can be used. The purpose of this chapter is to introduce: the advantages and disadvantages of Al as an aerospace material; the methods used to develop new high strength Al alloys; and the structure and objectives of the thesis.
1.1 **Advantages of Al alloys**

1.1.1 **Density**

One of the most notable properties of Al is its low density of 2.70 g cm\(^{-3}\). For comparison, the densities of Fe and Ti are 7.87 g cm\(^{-3}\) and 4.5 g cm\(^{-3}\), respectively \[1\]. Thus, the weight of a component manufactured from Al would be approximately 1/3 and 1/2 of those for components of the same geometry produced from Fe and Ti, respectively.

1.1.2 **Processing**

Another key advantage of Al is the ability to manufacture a variety of products by different processing techniques. Al is very easily cast because of its low melting temperature and viscosity, which can both be further reduced with additions of elements like Si and Zn. The direct chill-casting method can be used to produce Al bar stock in a range of sizes. Additionally, Al can be cast into more complex shapes by sand, investment, and die-casting. In terms of wrought product, Al is very malleable and exhibits high ductility. This allows for processing by extrusion or rolling into sheet and plate; both processes can be performed at either ambient or elevated temperatures. Moreover, Al alloys can be heat-treated to alter strength levels. Work-hardened material can be softened by annealing heat treatments, while other alloys can be precipitation-strengthened by artificial or natural aging. This wide range of processing schemes allows Al and its alloys to be manufactured into a variety of aircraft components such as housings, rivets, sheet skin, structural beams, and impellers.
1.1.3 Oxidation Resistance

Another important property of Al is that it readily reacts with oxygen in the atmosphere producing a thin layer of aluminum oxide. Because this oxide layer is impervious, it will protect the material underneath from further oxidation. However, if better oxidation resistance is required, the oxide layer can be thickened by a chemical treatment called anodizing. This is an electrolytic passivation process (using sulfuric or chromic acids) that causes an increase in the native oxide thickness, which can increase corrosion and wear resistance. In addition, chromate conversion coatings can be applied for added protection on top of the anodized layer [1].

1.2 Disadvantages of Al alloys

1.2.1 Limited Strength at Room and Elevated Temperatures

A major limitation of Al is that its ambient temperature strength is lower than that of other aerospace metals. Al alloys have tensile strengths ranging from 90 MPa for fully annealed alloys up to 600 MPa for alloys aged hardened to peak strength. These values are significantly lower than those for Ti alloys, which range from 280 – 1200 MPa, or for steels ranging from 330 – 1700 MPa. As such, in order to reduce stress levels to acceptable values components manufactured from Al would require much larger cross sections. This becomes problematic especially in regions where there are strict size constraints. Another issue is that Al alloys exhibit limited strength at elevated temperatures. Because Al has a melting point of ~660°C, it does suffer softening effects with increasing temperature at an earlier stage than other metals. Most Al alloys are
limited to operating conditions of up to 150°C, since prolonged exposure at higher temperatures will cause a rapid decline in strength [1].

1.2.2 Lack of Endurance Limit

Another important drawback of Al is its fatigue behavior. Many materials like Fe and Ni have what is called an “endurance limit.” This property is defined as the highest stress that a material can bear under cyclic loading where the probability of failure by fatigue will be zero. This property is very important because many components will experience loading and unloading stresses during flight. For example, the deflections of the wings and the vibrations of structural parts near the engines cause stress oscillations. Unfortunately, Al does not exhibit an endurance limit, meaning that Al components will eventually fail due to fatigue even if subjected to very low stress amplitude cyclic loadings. This further restricts the range of applications for which Al can be used in aircraft [1].

1.3 New High Strength Al alloys

There have been many attempts to develop new Al alloys with improved properties to further expand their use in aerospace applications, but the three most notable are: the development of ultra-fine grain microstructures through severe plastic deformation (SPD) processing (e.g. [2-6]); the formation of a high volume fraction of fine, coherent precipitate particles adopting the ordered L1₂ structure (e.g. [7-12]); and the suppression of crystallization to give stable (or metastable) amorphous phases (e.g. [13-17]). The latter approach is particularly interesting because, through careful control
of alloy chemistry and thermal-mechanical processing, it can be used to form a wide variety of unique microstructures including: amorphous single-phase (metallic glasses), FCC Al precipitates dispersed within an amorphous matrix, fully devitrified microstructures consisting of intermetallic particles dispersed within an FCC Al matrix, and quasi-crystalline precipitates dispersed within an FCC Al matrix. These types of microstructures are best summarized by Figure 1.1, which was published by Inoue et al in 2000 [18]. The left side of Figure 1.1 consists of schematic microstructures of the different materials that Inoue’s group has developed with the corresponding mechanical properties given on the right. It can be seen in Figure 1.1 that the materials consisting of an amorphous matrix exhibit tensile strengths that exceed those obtained in conventional Al alloys (~560 MPa) by a factor of two. However, one of the major drawbacks is that these amorphous materials are extremely brittle with elongations to failure of < 3%. Improvements in ductility (at the cost of strength) have been achieved in materials consisting of a matrix of FCC Al with a high volume fraction of precipitates or dispersoids (e.g. those containing quasi-crystalline precipitates [18-26] and fully devitrified materials [27-35]). However, the strengths of these materials are still substantially higher than those obtainable in conventional Al alloys making them prime candidates for high strength Al alloys.

Of the numerous Al-based systems studied, the ones that have received the most attention are Al-transition metal-rare earth (Al-TM-RE) alloys. These types of alloys have been known to form a variety of microstructures including those consisting of metastable amorphous single phases and quasi-crystals. The main focus of this thesis will be the detailed microstructural analysis of two alloys: 1) a devitrified Al-Ni-Co-Y-
Figure 1.1: Representative images of the different types of microstructures and their corresponding mechanical properties for different Al alloys developed using the amorphous phase as a precursor. Reproduced from ref [18].
Zr metallic glass alloy, and 2) an Al-Mn-Ce alloy shown in the literature to form quasicrystalline particles in an Al matrix.

1.4 **Objectives and Approach of this Study**

One of the major drawbacks in the development of the Al alloys mentioned in the previous section is that in order to form the desired metastable phases, one has to cool the material rapidly to suppress the formation of equilibrium phases. Cooling rates on the order of $10^6$ K/s are necessary to suppress crystallization, which cannot be achieved by traditional casting techniques. Instead, other methods like splat quenching, squeeze casting, melt spinning and gas atomization have been used. However, the dimensions of specimens produced by these processes are limited to between several hundred microns and a few millimeters. These size constraints prevent the manufacturing of aircraft components from these materials. Furthermore, without components made from these materials one cannot readily assess how the properties of these materials would behave under typical environmental and loading conditions experienced on an aircraft.

The purpose of this study was to address this issue of scalability. Instead of studying a series of compositions, only two compositions were chosen based upon promising results found in previous studies. These two alloys were then processed by powder metallurgical techniques. First, a fine powder was produced by gas atomization. This gave the cooling rates necessary to form the desired metastable phases, while allowing one to produce substantial quantities of material. The powder was then consolidated into Al cans and ram extruded at elevated temperature. This processing scheme results in a fully dense stock material that can be manufactured on an industrial
scale, where several meters of material with a diameter of several centimeters can be produced easily. With material of this size, one can now easily perform the types of detailed studies on the microstructure and mechanical properties of the material that are necessary when investigating a new aerospace material.

In this study, a detailed analysis was performed to investigate the stability of the phases present in these two alloys with heat treatment, and to relate the changes in the microstructure to the mechanical properties of these materials.

1.5 **Structure of this Thesis**

This thesis is divided into seven chapters: Chapters 2 and 3 contain a review of previous research on new high strength Al alloys via metastable vitreous intermediate Al-TM-RE alloys and the formation of metastable quasicrystalline dispersoids in Al-Mn-Ce alloys, respectively. Chapter 4, Materials and Experimental Methods, includes: the alloy compositions, the processes to which the alloys were subjected, and a summary of the specimen preparation and analytical techniques used. Chapters 5 and 6 contain the results, discussion and conclusions of the data obtained from the Al-Ni-Co-Zr-Y and Al-Mn-Ce alloys, respectively. Finally, Chapter 7 is a general summary of the important points arising from this study, including suggestions for future work.
Chapter 2: Metastable Vitreous Intermediates, Al-TM-RE Alloys

2.1 General Metallic Glass Formation

2.1.1 Preparation Techniques

2.2 Amorphous Al alloys

2.3 Partially Devitrified Al amorphous alloys

2.3.1 Crystallization of Amorphous Al Alloys

2.3.2 Effects of Nano-Scale Particles on Mechanical Properties

2.3.3 Proposed Mechanisms for Improved Mechanical Properties

2.4 Fully Devitrified Amorphous Al Alloys

2.4.1 Al-RE-TM Microstructures

2.4.2 Microstructural Stability

2.4.3 Microstructure/Mechanical Property Relationship

2.4.4 Deformability
2.1 **General Metallic Glass Formation**

The formation of a bulk metallic glass (BMG) is accomplished by suppressing the nucleation of the crystalline phase as a liquid metal is being cooled below its melting temperature. The driving force for the nucleation of the crystalline phase is a reduction in the free energy of the system, which is caused by the reduction in volume on going from the liquid to the solid state. However, metallic glasses have a lower driving force for crystalline nucleation because their change in volume from the liquid to solid state is much lower than that for other metals. The smaller change in free energy helps in the suppression of the crystalline phase and results in an amorphous metal.

Many groups have studied BMGs, but the most successful group is that led by Inoue in Japan. They have developed three empirical rules for alloys that form bulk metallic glasses; these alloys should:

1) Be multicomponent systems consisting of more than three elements.

2) Have significant differences in the atomic size ratios (above about 12%) between the main constituent elements.

3) Exhibit negative heats of mixing for the main constituent elements.

These rules are viewed as a general guide for the formation of metallic glasses and alloys produced using these three rules resulted in BMGs with high glass formability. A flow chart summarizing the key factors and mechanisms for high glass formability is shown in Figure 2.1. The idea behind these three rules is to chemically frustrate the system by: increasing the solid/liquid interfacial energy, which suppresses the nucleation of the crystalline phase; increasing the difficulty of atomic rearrangement by decreasing the
The constituent elements more than three kinds with large atomic size ratios above 12% and negative heats of mixing

Increase in the degree of dense random packed structure (topological and chemical points of view)

Formation of liquid with new atomic configurations and multicomponent interactions on a short-range scale

Increase of solid/liquid interfacial energy

Difficulty of atomic rearrangement (decrease of atomic diffusivity, increase of viscosity)

Necessity of atomic rearrangement on a long-range scale for crystallization

Suppression of nucleation of a crystalline phase

Increase of $T_g$

Suppression of growth of a crystalline phase

Decrease of $T_m$, Increase of $T_g / T_m$

Figure 2.1: Flow chart outlining the conditions and mechanisms necessary for the development of alloys with high glass formability. Reproduced from ref [36].
diffusivity; and creating large, complex unit cells which necessitates long scale atomic rearrangement for their crystallization leading to the suppression of the crystalline phase growth [36].

2.1.1 Preparation Techniques

During the early development of metallic glasses, the cooling rates required to suppress the formation of the crystalline phase were so high (on the order of $10^6$ K/s) that traditional casting techniques could not be used. Instead, other techniques, such as splat quenching, melt spinning and gas atomization had to be employed because these methods provided the necessary cooling rates. The experimental setup for splat quenching consisted of a cooled, curved Cu block, where droplets of the melt were dropped onto the block. This technique was later modified into a piston-anvil method, where the droplets are squeezed between a rapidly moving piston and anvil. Since the piston-anvil method provides heat extraction from two surfaces at once, the critical cooling rate could be obtained in much thicker specimens. Schematic diagrams of these two techniques are shown in Figure 2.2. The melt spinning technique is different from the previous two techniques in that a cooled, large, rotating Cu disk is used as the cooling medium. The melt is held above the disk in a crucible and is ejected onto the spinning disk by a high-pressure jet of gas. A schematic diagram of the melt spinning technique is shown in Figure 2.3. The result is a continuous strip of quenched material typically a few millimeters in width and tens of microns in thickness. In gas atomization, the melt is gravity feed down through a nozzle into a chamber. At the nozzle’s exit, the liquid stream is broken apart into droplets and cooled rapidly by high-pressure jets of inert gas.
Figure 2.2: Schematic diagrams of two splat quenching arrangements: (a) molten droplets falling on to a cooled, curved Cu block; (b) molten droplets squeezed between two moving pistons. Reproduced from ref [37].

Figure 2.3: Schematic diagram of the melt spinning technique. Molten material is ejected onto a rotating, cooled Cu disk that produces a constant strip of material. Reproduced from ref [38].
As the droplets cool into powder particles, they are collected at the bottom of the chamber. A schematic diagram of the gas atomization process is shown in Figure 2.4. However, for practical structural applications, components used are manufactured in sizes that far exceed the micron-sized specimens produced from the above-described techniques. The processing size limitation of BMGs has been reduced slightly over time as more complex alloys were developed that required relatively less critical cooling rates. These BMGs could be processed using the more traditional casting techniques used for crystalline metals, but the sizes of cast BMG bars are limited to tens of millimeters.

Subsequent thermal treatments on these amorphous alloys resulted in very intriguing microstructures along with further improvements in properties such as tensile strength. Inoue’s group published an illustrated summary, shown in Figure 2.5, of the different microstructures and associated mechanical properties for different Al alloys developed by their group. Although some of the microstructures do not contain any amorphous phases, many of them used the amorphous phase as a precursor, and through controlled processing and heat treatment these final microstructures were obtained. Some of these structures will be discussed in more detail.

2.2 Amorphous Al alloys

The development of amorphous Al alloys began during the mid 20th century. Some of the earliest reports of microstructures containing an amorphous phase were developed from binary Al- (Si, Ge, Cu, Ni, Cr, and Pd) [40-45]. In the early 1980s fully amorphous Al alloys were produced from Al-(Fe or Co)-B and Al-Fe-(Si or Ge) ternary systems, but these alloys were extremely brittle and exhibited low fracture strengths,
Figure 2.4: Schematic diagram of the gas atomization process. The molten material is gravity fed through a nozzle into a chamber. At the nozzle’s exit jets of high pressure inert gas break up the stream into droplets that cool rapidly into powders and are collected at the bottom. Reproduced from ref [39].
Figure 2.5: Representative images of the different types of microstructures and their corresponding mechanical properties for different Al alloys developed using the amorphous phase as a precursor. Reproduced from ref [18].
hence not suitable for structural applications [46, 47]. Then in the late 1980s Inoue’s group began producing higher strength amorphous Al-rich alloys which exhibited improved ductility such as Al-Ni-(Si or Ge), Al-Cu-V, and Al-Ni-Zr [48-51].

There are many different Al systems that have high glass formability, but the systems that have received most attention are those that are alloyed with transition metals (TM) such as: Ni, Fe & Co, and rare earths (RE) such as: La, Nd, Sm, Y, Ce & Gd [18, 52-55]. Such Al-TM-RE alloys can have tensile strengths as high as 1250 MPa in the amorphous state, which is approximately twice as high as the values achieved for conventional crystalline Al alloys aged to peak strength. However, these amorphous materials are still very brittle with elongations to failure of approximately 1 to 2 % [13-15, 17, 56].

2.3 Partially Devitrified Al Amorphous Alloys

The major advantage that amorphous Al alloys provide over conventional Al alloys is higher tensile strengths. However, further improvements were sought (especially in ductility), and it was found that partially devitrified Al amorphous alloys exhibited further improvements in mechanical properties such as tensile strength, ductility, fatigue, and wear resistance. These improvements were found to be associated with the formation of nano-scale fcc-Al particles in the amorphous matrix.

2.3.1 Crystallization of Amorphous Al alloys

There are two approaches that can be used to obtain a mixed crystalline-amorphous structure. One approach used is the precipitation of small crystals of fcc-Al
in the supercooled liquid. Then the remaining liquid solidifies into the amorphous matrix. This process requires the careful control of the cooling rate during processing. Melt spinning is the method typically used for this approach. However, this process is not very reproducible because many parameters have to be controlled, such as disk rotation speed and liquid flow rate. Another approach used is to first form a fully amorphous material, and then precipitate the fcc-Al crystals in the amorphous matrix by controlled heat treatments [51]. This second approach gives much better control and reproducibility over the precipitation of the nano-crystals and is the most widely used.

The crystallization of amorphous alloys occurs in several stages. Initial crystallization stages typically include the formation of fcc-Al nano-crystals within the amorphous matrix. The intermediate crystallization stages include the formation of several different stable and metastable intermetallic phases, along with coarsening of the fcc-Al crystals. Complete crystallization of the amorphous structure is seen after the last stage, which consists of fcc-Al grains, the stable intermetallics formed in previous stages, and a new intermetallic phase that forms during the last stage. For example, for Al-Ni-Y alloys, the first transformation to take place is the formation of nano-particles of fcc-Al. With continued heating, stable (and metastable) binary intermetallics form during the intermediate stages, and the final stage results in a fully crystalline microstructure consisting mainly of fcc-Al grains and a ternary intermetallic phase, while the binary intermetallic is the minority phase. Other alloys have shown other trends, such as Al$_{87}$Ni$_7$La$_6$ and Al$_{87}$Ni$_7$Ce$_6$, which do not form nano fcc-Al particles but rather form metastable intermetallics during the crystallization stages [57]. The next two sections will discuss the effects of these mixed structures on the mechanical properties.
2.3.2 **Effects of Nano-Scale Particles on Mechanical Properties**

The formation of these nano-scale fcc-Al particles has been shown to have a positive effect on the mechanical properties of amorphous materials. Fully amorphous alloys have tensile strengths as high as 1250 MPa. However, the precipitation of these nano-scale particles inside an amorphous matrix further increases their strengths. Choi et al produced partially devitrified Al$_{88}$Ni$_{10}$Nd$_2$, Al$_{88}$Ni$_9$Nd$_2$Fe$_1$, Al$_{88}$Ni$_{10}$Gd$_2$, and Al$_{88}$Ni$_9$Gd$_2$Fe$_1$ alloys with tensile strengths greater than 1500 MPa, where Al$_{88}$Ni$_{10}$Nd$_2$ achieved a maximum strength of 1980 MPa [58]. A plot of the effect of aging temperature on the tensile strength and elongation at fracture is shown in Figure 2.6. The microstructures of all four alloys contained fcc-Al particles approximately 10 nm in diameter. It is clear that there was a vast improvement in strength at an aging temperature between 400 and 480 K. For Al$_{88}$Ni$_{10}$Nd$_2$ alloy, plots of the micro-hardness, fracture strength, and fracture elongation versus volume fraction of fcc-Al particles are shown in Figure 2.7. This figure shows that peak strength and ductility was achieved with a volume fraction of 18%, while the hardness continues to increase with volume fraction. The other three alloys also exhibited peak properties at volume fractions of 18%. In addition, fracture elongation improved with the precipitation of these particles, where a 50% improvement in ductility can be seen in Figure 2.6 at the peak aging temperature [58].

Other studies also showed improvements in the hardness of partially devitrified alloys with increasing volume fractions of the fcc-Al particles. Rizzi and Battezzati performed microhardness measurements on three different alloys, Al$_{87}$Ni$_7$Nd$_6$, Al$_{87}$Ni$_7$La$_6$, and Al$_{87}$Ni$_7$Ce$_6$, aged at different temperatures up to 550°. The changes in
Figure 2.6: Aging temperature dependence of tensile fracture strength and fracture elongation in partially devitrified Al alloys. Reproduced from ref [58].
Figure 2.7: Changes in (a) micro hardness and (b) fracture strength and fracture elongation as a function of volume fraction of nano fcc particles in AlNi_{10}Nd_{2}. Reproduced from ref [58].
microhardness as a function of aging temperature for these three alloys is shown in Figure 2.8. As these alloys are aged, crystalline phases begin to form in the amorphous matrix, and these plots show that a general increase in hardness is achieved with an amorphous-crystalline mixed structure [57]. Also, the Al$_{87}$Ni$_7$Nd$_6$ alloy shows the greatest improvement in micro-hardness. Recall that the partially devitrified microstructures of Al$_{87}$Ni$_7$La$_6$, and Al$_{87}$Ni$_7$Ce$_6$ alloys do not contain nano fcc-Al particles but rather contain metastable intermetallics. On the other hand, the Al$_{87}$Ni$_7$Nd$_6$ alloy does contain nano fcc-Al particles, which is linked to the difference in hardness. (Proposed mechanisms for improvements are discussed in the next section.)

Inoue et al have shown that materials with this mixed microstructure have better elevated temperature tensile strength than fully amorphous alloys. For example, Figure 2.9 shows plots of the tensile strength and fracture elongation versus testing temperature for an Al$_{88}$Ni$_{10}$Nd$_2$ alloy in the amorphous state and with 8% volume fraction of fcc-Al nano-particles [58]. The fully amorphous alloy exhibits an interesting variation in strength. It has a sharp decrease from 1200 MPa to 960 MPa at 390 K, followed by a sharp increase, and then gradually decreases with temperature. The crystallization temperature of the alloy is 403 K, which is close to the temperature where the strength irregularity occurs. The authors explain that the decrease in strength is due to a weakening in the bonding force among the atoms before crystallization. The increase in strength that follows is due to the dispersion of the fcc-Al particles. On the other hand, the same alloy with an 8% volume fraction of the fcc-Al phase exhibited better properties with a continuous decrease in strength from 1450 MPa at 400 K to 960 MPa at 600 K [58]. Another alloy developed by Inoue’s group that exhibited enhanced elevated
Figure 2.8: Changes in micro hardness as a function of aging temperature for three alloys: Al$_{67}$Ni$_7$Nd$_6$, Al$_{67}$Ni$_7$La$_6$, and Al$_{67}$Ni$_7$Ce$_6$. Reproduced from ref [57].

Figure 2.9: Tensile strength and fracture elongation as a function of testing temperature for an Al$_{88}$Ni$_{10}$Nd$_2$ alloy in the amorphous state and with 8% $\nu_f$ of fcc-Al nano-particles. Reproduced from ref [58].
temperature strength was Al$_{88}$Ni$_{9}$Ce$_2$Fe$_1$, which had a 20% volume fraction of fcc-Al particles and maintained a tensile strength of 960 MPa at 600 K [59]. The elevated temperature strength of these amorphous alloys is 15 times greater than those exhibited by conventional, precipitation hardened Al alloys.

These mixed structures also have other improved properties such as compressive strength and wear resistance. A plot of wear resistance versus micro-hardness is shown in Figure 2.10, where different Al alloys are compared. The data shows that the hardness and wear resistance of the mixed amorphous-crystalline materials (labeled as nanophase composites) are superior to those of conventionally hardened Al alloys and early fully amorphous Al alloys [60].

2.3.3 Proposed Mechanisms for Improved Mechanical Properties

One proposed mechanism was that since the fcc-Al particles were so small that they were defect free and extremely strong. Therefore, these hard particles would act as strong barriers to deformation in the material. However, this is not believed to be the dominant mechanism because optimum strengths are obtained for particles coarsened to about 10-15 nm in diameter at a volume fraction of 20%. In addition, if these defect free particles were the main cause of strengthening, then a higher volume fraction should result in higher strengths, but the opposite trend is seen where volume fractions greater than 20% actually result in lower strengths and much more brittle materials. Kim et al proposed another strengthening mechanism using the Al-Ni-Y system as a model, which is the minority element enrichment of the amorphous matrix. As the fcc-Al particles form, the other elements are rejected into the surrounding amorphous matrix. As the fcc
Figure 2.10: Plot of the wear resistance as function of micro-hardness of various Al alloys. Reproduced from ref [60].
nano-particles form and reject Ni and Y, the Ni atoms diffuse very rapidly and are distributed homogenously in the amorphous matrix whereas the Y atoms diffuse much more slowly and tend to accumulate near the particle-matrix interface. As the local concentration of Ni and Y exceeds 20% these regions become brittle and act as nucleation sites for cracks. These results are in good agreement with results obtained for fully amorphous alloys wherein if the bulk minority elements composition exceeds 20% the materials become very brittle [61].

Although these partially devitrified alloys exhibit enhanced mechanical properties in comparison to traditional Al alloys, the biggest drawback is their extremely low ductility. Even though the precipitation of fcc-Al particles helps to improve ductility, these alloys only have elongations to fracture of 3%. Also, these materials require such high cooling rates that the maximum thickness of samples produced with an amorphous structure is limited to a few millimeters. These sizes are not suitable for practical structural applications. However, a compromise between strength and ductility was found by subsequent heat treatments to fully convert the material from the amorphous state to crystalline.

2.4 **Fully Devitrified Amorphous Al Alloys**

With sufficient heating, amorphous Al alloys can be fully devitrified into a crystalline material. In the crystalline state, these alloys exhibited much higher fracture elongations, but at the cost of slightly lower strengths. However, their strengths are still better than conventional Al alloys. A schematic microstructure of a devitrified alloy is
shown in Figure 2.5. These structures consist of fine fcc-Al grains and a high volume fraction of intermetallic compounds.

The development of high strength Al alloys through the devitrification of the amorphous state has been the focus of a Defense Advanced Research Projects Agency (DARPA) funded project called the Structural Amorphous Materials (SAM) program. The gas turbine engine company Pratt & Whitney is leading the SAM program. The alloys of interest have been Al-RE-TM systems. The processing approach used to produce these materials is powder metallurgy. The powder is formed using gas atomization, which provides the necessary cooling rates to form fully amorphous powder. Subsequent canning and extrusion consolidates the powder and fully devitrifies the amorphous structure into a bulk crystalline material. (A more detailed description of the processing of these alloys is given in Chapter 4).

2.4.1 \textit{Al-RE-TM Microstructures}

In these Al alloys, Rare earth metals like Y and Gd were used, and Transition metals used were Ni, Fe, and Co. Al-RE-TM alloys with compositions such as Al-Y-Ni, Al-Gd-Ni, Al-Y-Gd-Ni-Fe-Co, and Al-Ni-Y-(Fe, Co) were studied by our research group [27-35]. The microstructures that form after full devitrification of these alloys are generally similar to one another and are composed of three main features: fcc-Al grains, binary phase, and a ternary phase; representative TEM images are shown in Figure 2.11. The matrix consists of fcc-Al grains with sizes ranging from 100 to 600 nm in diameter [29]. The binary phase typically has an equiaxed morphology and its size ranges from 50 to 500 nm. The binary phase that forms is dependent on alloy composition. Vasiliev et
Figure 2.11: Bright field TEM images with inset SADPs showing the overall microstructures for: (a) Al-2.6Y-9.5Ni; (b) Al-4.5Y-10.1Ni; (c) Al-4.3Y-3.5Ni; and (d) Al-1.7Y-6.4Ni (all in at %). Reproduced from ref [29].
al studied four Al-Y-Ni alloys: Al-2.6Y-9.5Ni, Al-4.5Y-10.1Ni, Al-1.7Y-6.4Ni, and Al-4.3Y-3.5Ni (all in at%), and reported that the binary phase in the first three alloys was the Al$_3$Ni with the Fe$_3$C (Pnma) structure while the fourth alloy contained the Al$_3$Y phase which adopted the Pb$_3$Ba (R$^3$m) structure. TEM image, EDS, and diffraction analyses on the Al$_3$Ni and Al$_3$Y particles are shown in Figures 2.12 and 2.13, respectively [29]. However, the binary phases were the minority microstructural feature.

From the overall microstructures shown in the Figure 2.11, the majority of the particles are the ternary phase. The ternary phase appears to exhibit two different morphologies: equiaxed and rod-like, as shown in Figure 2.14. However, the ternary particles are actually plate shaped, so if they are viewed from the top the particles appear equiaxed and when viewed edge-on they appear as rods. The ternary phase was initially reported to be the Al$_{16}$Ni$_3$Y by Rykhal and Zarechnyuk, with other groups also claiming to have observed this phase [62-66]. However, only the symmetry and lattice parameters were reported. Raggio et al performed an extensive study on the phases formed in a series of ternary Al alloys subjected to long-term heat treatments and compared their data to the results reported by others in the literature. They did not observe the Al$_{16}$Ni$_3$Y phase in any of their experiments and discounted it as an equilibrium compound [67]. Vasiliev et al performed a detailed TEM analysis on the ternary phase. Using diffraction data, HRTEM, and computer simulations they determined that the ternary phase did not correspond to any known equilibrium phases, but instead was Al$_{19}$Ni$_5$Y$_3$, which adopted the orthorhombic Al$_{19}$Ni$_5$Gd$_3$ type structure [29, 68].

Similar results were also obtained from an Al-8Ni-7Gd (in at%) alloy [31]. In this case, the rare earth element Y was replaced with Gd, but the microstructure and the
Figure 2.12: Analysis of an Al$_3$Ni particle: (a) bright field TEM image, (b) EDS spectrum, (c) SADP obtained at the [001] zone axis, and (d) simulation of diffraction pattern at the same orientation. Reproduced from ref [29].
Figure 2.13: Analysis of an Al$_3$Y particle: (a) bright field TEM image, (b) EDS spectrum, (c) SADP obtained at the [-1-120] zone axis, and (d) simulation of diffraction pattern at the same orientation. Reproduced from ref [29].
Figure 2.14: Bright field TEM micrographs with inset SADPs obtained of the ternary phase present in: (a) Al-2.6Y-9.5Ni; (b) Al-4.5Y-10.1Ni; (c) Al-4.3Y-3.5Ni; and (d) Al-1.7Y-6.4Ni (all in at%). Reproduced from ref [29].
phases present are analogous to those observed in Al-Ni-Y systems. The bright field TEM image in Figure 2.15 shows the microstructure in the Al-8Ni-7Gd alloy: fcc-Al grains, the equiaxed binary phase Al\(_3\)Gd, and the plate-shaped ternary phase [31].

2.4.2 Microstructural Stability

The microstructures of these alloys appear to be very stable. Magdefrau et al studied the effect of heat treatment on the microstructure of an Al-3Y-3Gd-5Ni-1Fe-1Co (at%) alloy [28]. Figure 2.16 is a bright field TEM image of the initial microstructure which exhibits the same features as the other alloys: fcc-Al grains, binary particles of Al\(_3\)(Y,Gd) and ternary particles of Al\(_{19}\)(Ni,Fe)\(_3\)(Y,Gd)\(_3\). The heat-treated samples contained the same phases and morphologies and were only coarsened versions of the initial microstructure. TEM images of this alloy heat-treated for 5 h at 450°C and 550°C are shown in Figure 2.17 [28]. A summary of the particle dimensions in the as extruded and heat treated samples is shown in Table 2.1. Taking into consideration the high homologous temperatures used for heat-treating, the particles coarsen very slowly. In addition, Table 2.2 shows the results of a detailed statistical analysis performed on the variation of the lengths and widths of the rod-like ternary phase in samples heat-treated at various temperatures between 400 and 550°C for 5 h. Although the sizes of the rod increase by an order of magnitude after the 550°C heat treatment, the aspect ratio for the rods remains constant at ~6 in all the samples studied. These results suggest that this is the equilibrium morphology for these particles [28].
742 A.L. Vasiliev et al. / Intermetallics 13 (2005) 741–748

Figure 2.15: Bright field TEM image of the overall microstructure in an Al-Ni-Gd alloy with examples of phases indicated: (a) fcc-Al grains; (b) equiaxed Al$_3$Gd particles; (c) rod-like ternary particles; (d) equiaxed ternary particles. Reproduced from ref [31].
Figure 2.16: Bright field TEM image of the initial microstructure in an Al-3Y-3Gd-5Ni-1Fe-1Co (at%) alloy with the three main phases indicated: (a) fcc-Al grains; (b) ternary particles Al$_5$(Ni,Fe)$_3$(Y,Gd)$_3$; (c) binary particles Al$_3$(Y,Gd). Reproduced from ref [28].
Figure 2.17: Bright field TEM images of the microstructures exhibited by Al-3Y-3Gd-5Ni-1Fe-1Co (at. %) samples heat-treated for 5 h at: (a) 450 °C; (b) 550 °C. Reproduced from ref [28].
Table 2.1: Summary of the dimensions of the rod-like ternary phase, Al$_{19}$(Ni,Fe)$_5$(Y,Gd)$_3$, in Al-3Y-3Gd-5Ni-1Fe-1Co (at%) alloy in the as-extruded sample and in samples heat treated for 5 h at 400 and 550°C. Reproduced from ref [28].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Morphology</th>
<th>Particle dimensions (nm)</th>
<th>AR</th>
<th>400 °C</th>
<th>550 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/FCC</td>
<td>Equi-axed</td>
<td>100–500</td>
<td>100–500</td>
<td>200–2000</td>
<td></td>
</tr>
<tr>
<td>Al$_3$(Ni,Fe)$_5$(Y,Gd)$_3$/Al$_5$Ni$_3$Gd$_3$-type</td>
<td>Rod-like</td>
<td>100–500 (L)</td>
<td>100–500 (L)</td>
<td>300–3000 (L)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20–80 (W)</td>
<td>20–50 (W)</td>
<td>100–300 (W)</td>
<td></td>
</tr>
<tr>
<td>Al$_3$(Y,Gd)/Ni$_3$Sn-type</td>
<td>Equi-axed</td>
<td>20–100</td>
<td>50–200</td>
<td>50–600</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Summary of the lengths and widths of the rod-like ternary phase, Al$_{19}$(Ni,Fe)$_5$(Y,Gd)$_3$, in Al-3Y-3Gd-5Ni-1Fe-1Co (at%) samples heat treated for 5 h between 400 and 550°C. Reproduced from ref [28].

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>400</th>
<th>450</th>
<th>475</th>
<th>500</th>
<th>525</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$ (nm)</td>
<td>299</td>
<td>491</td>
<td>967</td>
<td>1709</td>
<td>1628</td>
<td>2179</td>
</tr>
<tr>
<td>$W$ (nm)</td>
<td>39</td>
<td>85</td>
<td>165</td>
<td>263</td>
<td>272</td>
<td>368</td>
</tr>
</tbody>
</table>
2.4.3 Microstructure/Mechanical Properties Relationship

Magdefrau et al also studied the effect of these heat-treatments on the material’s micro-hardness [28]. The initial hardness for the as-extruded sample was 303 HV. They then obtained micro-hardness measurements from samples heat-treated between 400 and 550°C for 0.5, 2.5 and 5 h. A plot of the variation of hardness with temperature and time is shown in Figure 2.18 [28]. The plots show that there was an initial sharp decrease at each temperature, followed by a gradual decrease with prolonged exposure. In addition, they looked at the relationship between the hardness and ternary phase particle size and found that there is a strong linear correlation, which is shown in Figure 2.19. For typical metals the movement of dislocations causes plastic deformation. However, if dislocations come across any obstacles (e.g. precipitate particles) they will be forced to either cut through or loop around the particles. This disruption to dislocation movement leads to strengthening/hardening of metals by mechanisms such as Orowan or Hall-Petch type strengthening. For a constant volume fraction and fixed aspect ratio of particles, the inter-particle separation, $\lambda$, is directly proportional to the particle dimensions. In Orowan and Hall-Petch strengthening, the material hardness should be inversely proportional to $\lambda$ and $\lambda^{1/2}$, respectively. Recall that the data in Figure 2.19 shows a linear relationship between hardness and particle size. Since these results are not consistent with those expected from Orowan and Hall-Petch strengthening, it implies that dislocation/particle interactions are not the controlling factor, especially in systems where the particle sizes are on the same order of magnitude as the Al grains [28].
Hardness values were obtained from each sample by taking the mean size of eight separate indentations. The variation in hardness with heat treatment temperature and time is shown in Fig. 4. At each temperature there is a rapid initial decrease in hardness, followed by more gradual softening. After heat-treating for 5 h at 400, 450, 475, 500, 525 and 550 °C, the hardness values were 278, 262, 237, 200, 189 and 158 Hv, respectively. It is interesting to note that a very strong linear correlation was found between these values and widths of the rod-like Al\textsubscript{19}(Ni,Fe)\textsubscript{3}(Y,Gd)\textsubscript{3} particles as shown in Fig. 5.

The mean aspect ratio for the rods is roughly constant at 2.18 ± 3% by choosing an indenter load for which the indentation size exceeded that of the largest microstructural features by at least an order of magnitude. The hardness of the initial extrusion was 303 Hv, which is consistent with Orowan or Hall–Petch type strengthening for which one would expect hardness to be inversely proportional to the constant volume fraction of randomly-oriented particles with a fixed aspect ratio, the inter-particle separation, and widths.

### Table 1

<table>
<thead>
<tr>
<th>Phase Morphology</th>
<th>Particle dimensions (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/FCC Equi-axed</td>
<td>100–500 100–500 200–2000</td>
</tr>
<tr>
<td>(Ni,Fe)_\textsubscript{3}Y</td>
<td>20–50</td>
</tr>
<tr>
<td>(Y,Gd)/Ni</td>
<td>20–100 50–200 50–600</td>
</tr>
<tr>
<td>Al</td>
<td>100–500 100–500 200–2000</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>AR 400</th>
<th>AR 450</th>
<th>AR 475</th>
<th>AR 500</th>
<th>AR 525</th>
<th>AR 550</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>450</td>
<td>475</td>
<td>500</td>
<td>525</td>
<td>550</td>
</tr>
<tr>
<td>299</td>
<td>491</td>
<td>967</td>
<td>1709</td>
<td>1628</td>
<td>2179</td>
</tr>
</tbody>
</table>

Figure 2.18: Plots of the hardness taken from Al-3Y-3Gd-5Ni-1Fe-1Co (at%) alloys heat-treated at various temperatures and times. Reproduced from ref [28].

Figure 2.19: Plots of the variation in hardness with the length and width of the rod-like Al\textsubscript{19}(Ni,Fe)\textsubscript{3}(Y,Gd)\textsubscript{3} particles in an Al-3Y-3Gd-5Ni-1Fe-1Co (at%) alloy. Reproduced from ref [28].
2.4.4 Deformability

In a more recent study conducted by the present author, the deformability of a powder processed Al-6.1Ni-1.0Co-4.7Y (at.%) alloy consolidated by warm extrusion was investigated [27]. As-extruded sections of material were subjected to a series of forging upsets: 43%, 64% and 84% parallel to the extrusion axis. The microstructure in the as-extruded material was a two-phase mixture of FCC Al with a dispersion of Al$_{19}$Ni$_5$Y$_3$ plates with a volume fraction of $V_f \approx 44\%$. Diffraction analysis revealed that the [100], [010] and [001] directions in the 19-5-3 structure lay parallel to the length (major axis), width, and thickness (minor axis) of the plates, respectively, which is consistent with previous observations [28-35].

Tensile tests were performed on each of the samples. Figure 2.20 is a plot of the mean values of tensile data versus forging upset. Two sets of data are shown for the as-extruded material, the higher values are those obtained from tensile specimens cut with the tensile axis parallel to the extrusion direction, while the lower values and those from the upset forged samples are from tensile specimens cut in the perpendicular direction. Tensile tests performed on the extrudate revealed that the material was highly anisotropic; exhibiting yield strength and strain to failure of 676 MPa and 5.0%, respectively parallel to the extrusion direction as compared to 521 MPa and 0.62%, respectively perpendicular to the extrusion direction. For the samples perpendicular to the extrusion direction (i.e. the data points connected with the line in Figure 2.20), a significant increase in the yield strength and strain to failure is observed with upset forging from 521 MPa and 0.62% at 0% upset to 713 MPa and 3.4% at 84% upset.
Figure 2.20: Mean values of tensile data from the as-extruded (0% upset) and upset forged samples. The squares are the mean values of yield strength and the circles are the mean elongations to failure. For clarity, the variability in these values is shown in table 2.3 rather than as error bars on the figure. Two sets of data are given for the as-extruded (0% upset) material: the higher values are from samples cut with the tensile axis parallel to the extrusion direction. The lower values and those from the upset forged samples are from samples cut with the tensile axis perpendicular to the extrusion/forging axis, and the lines through these values are intended as a guide to the eye. Reproduced from ref [27].
The corresponding microstructural changes were investigated by electron microscopy, and a representative selection of the data is presented in Figure 2.21. Here the BSE SEM images (Figures 2.21(a), (d), (g), and (j)) are presented with the vertical axes aligned with the extrusion/forging axis, and the bright features correspond to the 19-5-3 phase. The BF TEM images (Figures 2.21(b), (e), (h), and (k)) were obtained with the electron beam direction parallel to the extrusion/forging axis, and in these images the 19-5-3 phase are the dark features. Measurements of the 19-5-3 particles from each of the samples were obtained using BF TEM images. Particle size distributions of the maximum Feret diameter, $d_f$, are presented in Figures 2.21(c), (f), (i), and (l). There was no evidence of the particles breaking up even after forging to an upset of 84%. Instead, the 19-5-3 plates appear to rotate during upset forging.

Further evidence for plate rotation was obtained from tomographic reconstructions generated from stacks of 200 SE SEM images acquired by FIB serial sectioning. One example of a reconstruction is shown for each of the 0, 43, 64, and 84% upset forged samples in Figure 2.22. Here the bounding boxes represent a volume of 2 x 2 x 3 µm with the long axis parallel to the extrusion/forging axis, and perspective projections of the reconstruction parallel and perpendicular to this direction are shown. It can be clearly seen that in the as-extruded and the 43% upset forged material the major axis of the 19-5-3 plates is aligned with the extrusion direction. However, a more significant change in the plate orientation is observed for the 64% and 84% upset forged materials such that the plates in the 84% upset material have rotated by 90° with respect to those in the as-extruded material. If one were to refer back to the mechanical property data shown in Figure 2.20, it was noted that in both cases where the tensile axis was
Figure 2.21: Microstructural data obtained from samples: (a)-(c) as-extruded; (d)-(f) 43% upset; (g)-(i) 64% upset; (j)-(l) 84% upset. In each case these are: BSE SEM images of samples sectioned parallel to the extrusion/forging axis and oriented with this axis parallel to the vertical edges of the images, BF TEM images obtained from samples sectioned perpendicular to the extrusion/forging axis, and plots of particle diameter ($d_F$) measured from BF TEM images using the maximum Feret diameter approach, respectively. The mean values of $d_F$ are $130 \pm 39$, $137 \pm 40$, $143 \pm 46$, and $164 \pm 53$ nm for the 0, 43, 64, and 84 % upset samples, respectively. Reproduced from ref [27].
Figure 2.22: Tomographic reconstructions of selected 19-5-3 plates within 2 x 2 x 3 µm volume of the alloy samples: (a), (b) as-extruded (0% upset); (c), (d) 43% upset; (e), (f) 64% upset; (g), (h) 84% upset. In each case these are projections of the reconstruction parallel and perpendicular to the extrusion/forging axis, respectively. Reproduced from ref [27].
parallel to the major axis of the 19-5-3 plates, that the material exhibited an enhanced
tensile strength, much like a short fiber reinforced composite. The observations from this
study indicate that these materials can constitute truly deformable high strength metal-
matrix composites.
Chapter 3: Quasicrystalline reinforced Al-Mn-Ce Alloys

3.1 Quasicrystals: Discovery and Scientific Importance

3.2 Single-Phase Quasicrystals

3.2.1 Formation Regime and Microstructure

3.2.2 Mechanical Properties

3.3 Al-Mn-Ce Alloys

3.3.1 Formation Regime and Microstructure

3.3.2 Mechanical Properties
Chapter 3: Quasicrystalline reinforced Al-Mn-Ce Alloys

3.1 Quasicrystals: Discovery and Scientific Importance

In the field of crystallography, it is well understood that a crystal can only exhibit one-, two-, three-, four-, and six-fold rotational symmetry if it is to maintain translational symmetry (which is the main criterion for periodic structures) [69]. Therefore, it was understood that standard crystallographic notions forbade five-fold rotational symmetry. However, this concept was challenged by the publication of two major, controversial papers by Shechtman et al [19, 70]. Shechtman was performing work on rapidly solidified binary Al-Mn systems. While investigating these systems he noticed the formation of ‘spherulites’ in melt-spun specimens, which exhibited even more uncharacteristic electron diffraction spot patterns. Figure 3.1 is a representative BF TEM image of the overall microstructure in a rapidly solidified Al₆Mn alloy. The microstructure consists mainly of one phase with grains exhibiting elongated dendrites radiating from a central core as can be seen more clearly in the BF TEM image in Figure 3.2. However, the more interesting aspect of these grains is revealed by the electron diffraction patterns. Figure 3.3 is a representative selected area diffraction pattern obtained from one of these grains, where one can clearly see that the pattern exhibits 5-fold symmetry. Similar five-fold patterns were obtained using convergent beam diffraction as the example shown in Figure 3.4. Patterns such as these could be obtained from any region within these grains, meaning that these features are not isolated artifacts within these grains. Tilting experiences in the TEM revealed that there were other five-fold type patterns along with characteristic two- and three-fold patterns for this phase. A sequence of selected area diffraction patterns obtained from one grain tilted a various
Figure 3.1: Representative BF TEM image obtained from a rapidly solidified $\text{Al}_6\text{Mn}$ alloy showing the overall microstructure. Reproduced from ref [19].

Figure 3.2: Representative BF TEM image obtained from a rapidly solidified $\text{Al}_6\text{Mn}$ alloy on an individual spherulite. Reproduced from ref [19].
Figure 3.3: Representative SADP obtained from an individual spherulite like the one shown in Figure 3.2. Reproduced from ref [19].

Figure 3.4: Convergent beam electron diffraction pattern obtained from an individual spherulite grain like the one shown in Figure 3.2. Reproduced from ref [19].
systematic tilt angles is presented in Figure 3.5. Here the tilt angles are measured starting from the five-fold pattern at the bottom right of the figure. Shechtman proposed these patterns could be obtained from a structure that consisted of edge-sharing icosahedrons. Based on these assumptions, simulations were performed to calculate the kinematical diffraction patterns expected from this phase. Figure 3.6 shows the expected five-, three-, and two-fold patterns from the icosahedral phase. The spot patterns observed in Figure 3.5 matched up very closely to those obtained from these simulations, further reinforcing Shechtman’s claim that these microstructural features constitute a previously unreported phase that is neither amorphous or crystalline, but is capable of producing sharp diffraction peaks. This work was pivotal in opening up the new field of quasicrystals, and the impact was of this discovery led to him being awarded in the Nobel Prize in Chemistry in 2011 for his discovery.

3.2 **Single-Phase Quasicrystals**

Although Shechtman received a lot of criticism about this work, it was not very long after his discovery that several other groups from around the world began to also report the presence of quasicrystals in several different alloy systems [71-73]. Ever since, there have been extensive studies aimed at understanding their properties, and finding ways to utilize them in practical applications.

3.2.1 **Formation Regime and Microstructure**

In binary Al-Mn alloys, quasi-crystals have been reported in alloys with Mn concentrations ranging from 3 – 23 at. % [20, 21, 74, 75]. Single-phase (or monolithic)
Figure 3.5: Series of SADPs obtained from one quasicrystalline grain in a rapidly solidified binary Al-Mn alloy at various tilt angles. The tilt angles below each diffraction pattern is measured relative to the five-fold pattern at the bottom right of the figure. Reproduced from ref [19]
Figure 3.6: Simulated kinematical diffraction patterns of a grain exhibiting the quasicrystalline structure along the: (a) five-fold axis; (b) three-fold axis, tilted 37.38° away from five-fold axis; and (c) two-fold axis, tilted 58.29° away from five-fold axis. Reproduced from ref [19].
quasi-crystals have been observed in the higher Mn concentrations approximately at 22 – 23 at. % [75]. For Mn concentrations ranging between 14 and 22 at. %, the microstructures have been reported to consist mainly of quasi-crystalline grains, FCC Al, and occasional grains of the equilibrium Al-Mn intermetallic phase Al₆Mn [23, 76]. With lower Mn concentrations (e.g. < 14 at.%), the proportion of the quasicrystalline grains (as one would expect) decreases such that they become surrounded by a matrix of FCC Al [19]. At Mn concentrations greater than 23 at. %, the icosahedral phase appears to become unstable and instead the formation of equilibrium Al-Mn phases such as Al₃Mn are preferred [75].

The distribution and morphology of icosahedral quasi-crystals that are formed in binary Al-Mn systems are very similar to those shown in Figures 3.1 and 3.2. The quasicrystalline grains tend to adopt an equiaxed morphology with a dendritic structure such that the dendrite arms radiate from the center of each individual grain [19, 75]. In the case for Mn concentrations less than 22 at. %, these grains are surrounded by a thin film of FCC Al, which increases in volume fraction with decreasing Mn content, such that for Mn concentrations less than 14 at.% the quasi-crystals are essentially in a matrix of FCC Al. Figure 3.7 contains more examples of similar microstructures obtained in two rapidly solidified Al-Mn alloys. Figures 3.7(a) and (b) are representative BF TEM images obtained from Al-14.3Mn and Al-22.5Mn (both in at.%) alloys, respectively [75]. The microstructure for the Al-14.3Mn (at.%) alloy in Figure 3.7(a) exhibits the same classical features for quasi-crystals with the spherulitic morphology and the dendritic internal structure. The bright regions surrounding these grains is the FCC Al phase. For the Al-22.5Mn at.% alloy, Figure 3.7(b), the microstructure is slightly different such that the
grains do not exhibit such a prominent dendritic structure and the grains are slightly finer than those in the Al-14.3Mn (at.%) alloy (Figure 3.7(a)). The microstructure for the 22.5Mn at.% alloy is completely comprised of icosahedral grains, where in Figures 3.7(c), (d), and (e) one can see the SADPs obtained from these grains which exhibit the characteristic five-, three-, and two-fold symmetry patterns expected from an icosahedral quasi-crystal. These morphologies and diffraction patterns are consistently found for the icosahedral phase in other Al systems, for example Al-V as shown in Figure 3.8.

High-resolution TEM has also been used to investigate the structure of quasi-crystals, with one of the earliest reports coming out of Inoue’s group by Hiraga et al [20]. Here they presented a high-resolution micrograph obtained with the beam direction parallel to the five-fold axis, as shown in Figure 3.9, from a rapidly solidified Al-14.3Mn (at.%) alloy. One can clearly see the five-fold symmetry in this image. High-resolution images such as these were used to study the atomic arrangement perpendicular to the five-fold axis and proposed a structure model of edge connecting icosahedrons that would account for the atomic structure observed by HRTEM. A schematic of the proposed icosahedron is presented in Figure 3.10, which consists of 12 Al atoms located on the vertices surrounding a Mn atom in the center. A more recent study conducted by Saksi et al [74] used high energy XRD and extended X-ray absorption fine structure (EXAFS) to investigate the atomic coordination in a melt spun Al-2.5Mn (at.%) alloy. The results suggest that for the icosahedral phase, the Mn atoms have a coordination of 10, meaning that instead of being located in the center of the icosahedron, the Mn atoms may in fact be located on two of the vertices as shown in Figure 3.11 [74].
Figure 3.7: Representative BF TEM images obtained from melt spun (a) Al-14.3Mn at. % and (b) Al-22.5Mn at. % alloys, and SADPs obtained from the Al-22.5Mn at. % along the (a) five-fold, (b) three-fold, and (c) two-fold axes. Reproduced from ref [75].
Figure 3.8: Representative BF TEM images obtained from melt spun (a) Al-14.3V at. % and (b) Al-17.5V at. % alloys, and SADPs obtained from the Al-17.5V at. % along the (a) five-fold, (b) three-fold, and (c) two-fold axes. Reproduced from ref [75].
Figure 3.9: Representative (a) high resolution TEM image and (b) corresponding electron diffraction pattern obtained from a melt spun Al-14.3Mn at. % alloy along the five-fold axis. Reproduced from ref [20].
In this work we present our structural study upon Al–5Mn alloy in as-quenched form EXAFS signal analysis 10, therefore one can assume exclusive distance/pattern of icosahedral quasycrystalline phase. In icosahedron body atom is located in the center of the icosahedron. The atom located in pentagon cups) or in centre of the body. The atom located in pentagon cups) or in centre of the body. The coordination of Al atoms remains constant, while only the symmetry and parameters of Al atoms changes. 

Conclusions

From the local atomic structure refinement follows that the total number of Al coordinating one Mn atom in average is 10, regardless of annealing, while the Mn–Al interatomic distance decrease significantly (7%) after pre-annealing at 773 K. Similarly, the value of the mean-square displacement significantly decreases after high temperature annealing. One can therefore assume exclusive distance/pattern of the icosahedral quasycrystalline phase. In icosahedron body Mn atom is located in the center of the icosahedron. Reproduced from ref [20].

Figure 3.10: Structural model for fundamental icosahedron proposed by Hiraga et al based on HRTEM images obtained from a melt spun Al-14.3Mn at. % alloy. The vertices are occupied by Al atoms and Mn atom is located in the center of the icosahedron. Reproduced from ref [20].

Figure 3.11: Structural model for fundamental icosahedron proposed by Saksi et al based on EXAFS measurements obtained from a melt spun Al-2.5Mn at. % alloy. Mn atoms occupy two of the icosahedron’s vertices and Al atoms occupy the remainder. Reproduced from ref [74].
3.2.2 Mechanical Properties

Since the discovery of quasi-crystals, there has been considerable interest in their mechanical properties. The first reported evidence of dislocations in quasi-crystals was by Hiraga et al in an icosahedral Al-Mn-Si alloy using high-resolution electron microscopy [77]. A HRTEM image of one such dislocation is presented in Figure 3.12 along with the burgers circuit. Takeuchi et al have shown that at room temperature dislocations in quasi-crystals are largely sessile, which explains why quasicrystals exhibit such high hardness and strength but also causes them to be extremely brittle in monolithic form [78]. Hardness tests on single crystal Al$_{62}$Co$_{15}$Cu$_{20}$Si$_{3}$ decagonal quasicrystals were performed by Wittmann et al in which they reported a value of 9.5 GPa (968 VHN) [79]. This value compared to that of single crystal Si (10 GPa, 1000 VHN) and to age hardened Al (H = 1.8 GPa, 180 VHN) shows the remarkable enhancement in hardness for an Al based material. Wittmann et al used the measured hardness values to calculate the fracture toughness and found it to be approximately $K_{IC} = 1.0$ MPa m$^{1/2}$, which is significantly lower than that obtained for conventional Al alloys (e.g. 30 MPa m$^{1/2}$ [80]).

The poor fracture toughness and brittleness of the material can be seen in Figure 3.13, which is a representative SEM image of a Vickers hardness indent on the material. Here one can see the long cracks that formed adjacent to the indent, whereas in more ductile materials the region surrounding the indent is void of cracks with an plastically deformed region. A study conducted by Bhaduri and Sekhar also reported similarly low toughness values for an Al-Cu-Li quasicrystalline alloy [81]. In a review of dislocations in quasicrystals by Edagawa [82] several examples of Vickers hardness values are listed for different Al based icosahedral and decongonal quasicrystals where the hardness ranges
Figure 3.12: High resolution TEM image obtained from a rapidly solidified Al\textsubscript{74}Mn\textsubscript{20}Si\textsubscript{6} alloy showing a dislocation in an icosahedral grain. The lines drawn on the figure are the burgers circuits formed with parallel lines along the A and B directions. Reproduced from ref [77].

Figure 3.13: Representative SEM image of a Vickers hardness indent obtained from an Al\textsubscript{62}Co\textsubscript{12}Cu\textsubscript{20}Si\textsubscript{3} alloy. The three dark lines adjacent to the indent are cracks that formed. Reproduced from ref [79].
from 5.1 to 9.8 GPa (520 – 1000 VHN), which are comparable to those obtained for Si, various metallic glasses, and Al₂O₃.

Further work has been performed to investigate the mechanical behavior at elevated temperature. At testing temperatures at approximately 0.8T_{\text{melting}}, quasicrystals have been observed to exhibit enhanced ductility [83-85]. At first this phenomenon was not attributed initially to dislocation motion. However, a study by Wallgarten et al [86] on Al₇₀Pd₂₁Mn₉ revealed the first evidence of dislocation glide in quasicrystals at elevated temperature. A subsequent study by Wallgarten et al showed the first direct evidence of dislocation glide using in-situ TEM [87]. However, an interesting phenomenon that occurs is that quasicrystals do not exhibit strain hardening but instead become softer with deformation. Two examples of true stress versus true strain curves are presented in Figures 3.14 and 3.15 for an Al-Pd-Mn quasicrystal tested at elevated temperature under compressive loads [82, 88]. One can see that after the material enters the plastic deformation zone that there is a considerable drop in the stress by at least a factor of 2. With increased strain, the material then begins to develop strain-hardening response, albeit a small one. Room temperature investigations of the hardness for an Mg-Zn-Ho quasicrystalline alloy also reveal a work softening effect [89]. Figure 3.16 is compiled summary by Edagawa of the effect of temperature on compressive yield strength for several different quasicrystalline materials [82]. One can see that the strength of the materials decrease with increasing temperature as one would expect if dislocation glide is to become easier for these materials at elevated temperature. Although many reports note that there was either no anisotropy or a weak relationship between orientation and hardness [79, 81, 82, 90-92], a more detailed study by
Figure 3.14: Plot of the true stress versus true strain measured in compression at testing temperatures of 993 K and 1013 K for a single grain Al-Pd-Mn icosahedral alloy. Reproduced from ref [82].

Figure 3.15: Plot of the true stress versus true strain measured in compression at a testing temperature of 963 K for a single grain Al-Pd-Mn icosahedral alloy. Reproduced from ref [88].
Figure 3.16: Plot of the yield stress measured in compression versus testing temperature for various icosahedral alloys: open circle Al-Pd-Mn; solid circle Al-Cu-Fe; cross Al-Cu-Ru; open triangle Al-Li-Cu; solid triangle Mg-Zn-Gd; solid square Mg-Zn-Y. Reproduced from ref [82].
Yokoyama et al did show some significant differences in hardness with orientation and temperature. Yokoyama et al [93] performed hardness tests on an Al$_{70}$Pd$_{20}$Mn$_{10}$ alloy along the two-, three-, and five-fold axes. A plot from their study is presented in Figure 3.17, which presents the hardness values obtained along the different axes versus temperature. The hardness values obtained along the three-fold axis are greater than both the values measured along the two- and five-fold axes up to temperatures of 600 K. However, above 600 K, the hardness measured along the five-fold axis is the greatest, while the other two axes exhibit similar hardness values.

As dislocation movement becomes easier at elevated temperature, quasicrystals also exhibit enhanced ductility and increased fracture toughness. Work performed by Yokoyama et al [93] on the elevated temperature properties of an Al$_{70}$Pd$_{20}$Mn$_{10}$ alloy has shown improvements in both parameters. Figure 3.18 is a plot of the fracture toughness measured along the two-, three-, and five-fold axes versus testing temperature. There is no significant difference observed in the fracture toughness with orientation. However, the toughness does increase drastically from approximately 1 MPa m$^{1/2}$ at room temperature to over 10 MPa m$^{1/2}$ at 700 K. A similar increase in ductility was observed for samples tested in compression. Figure 3.19 is a plot of several nominal stress/strain curves measured at different testing temperatures. At room temperature, the material fails in a brittle manner at a strain less than 0.2%. With increasing temperature, the elastic modulus exhibits a decrease in value (i.e. decrease in the slope) from 200 GPa to 60 GPa while the strain to failure increases drastically to 1% for the sample tested at 973 K. At higher temperatures, the modulus does not vary much, but the strain to failure continues to increase to values above 1.8%. Although it is clear that these are marked
Figure 3.17: Plot of the mean values of Vickers hardness versus testing temperature measured from an Al$_{70}$Pd$_{20}$Mn$_{10}$ alloy along the two-, three-, and five fold directions. Reproduced from ref [93].

Figure 3.18: Plot of the mean values of fracture toughness versus testing temperature measured from an Al$_{70}$Pd$_{20}$Mn$_{10}$ alloy along the two-, three-, and five fold directions. Reproduced from ref [93].
Figure 3.19: Compressive stress/strain curves obtained from an Al$_{70}$Pd$_{20}$Mn$_{10}$ alloy tested at room temperature, 573, 773, 973, 1023, and 1073 K. Samples were tested along the three-fold axis. Reproduced from ref [93].
improvements in ductility and fracture toughness, these values are still significantly lower than those obtained for conventional Al alloys. These extremely low fracture toughness and ductility values make single-phase quasicrystalline materials completely unsuitable for aerospace structural applications.

3.3 **Al-Mn-Ce Alloys**

Although bulk and single quasicrystalline materials offer vast improvements in hardness and strength as compared to conventional Al alloys, their poor ductility and fracture toughness limits their use for structural engineering applications. While these characteristics may preclude the use of bulk quasi-crystals for structural applications, they are good candidates as second phases for precipitation/displacement strengthening in Al alloys. However, one issue is that many quasicrystalline materials tend to require high concentrations of solute elements, like Mn, Cr, Co, Pd, Y and Gd in order to form suitable proportions of the quasicrystalline phase [94]. If one has to add high amounts of heavier elements in order to form these microstructures, it inevitably increases the alloy density (i.e. weight). There has been extensive research performed at identifying low solute alloy compositions that will exhibit easy formation of quasicrystalline particles and at sufficiently high volume fractions to offer improvements in strength. One of the most notable alloy systems is that based on Al-Mn-Ce.

3.3.1 *Formation Regime and Microstructure*

It has been shown that the addition of rare earth elements such as Ce could promote the formation of quasi-crystalline phases in Al-Mn alloys [18, 22, 24-26, 95-99].
Inoue et al performed an extensive study on several different Al-Mn-Ce compositions [26]. Figure 3.20 is a plot of all of the compositions investigated in their study where the vertical and horizontal axes correspond to the Ce and Mn concentrations in at. %, respectively. Phase field boundaries are drawn in order to more clearly delineate the different microstructures observed in the melt spun ribbons. In addition, next to each data point is the corresponding decomposition (or crystallization) temperature in degrees Kelvin. The as-spun ribbons can consist of a solid solution of FCC Al, FCC Al + quasicrystals, quasicrystals + amorphous, FCC + amorphous and fully amorphous microstructures. One can see here that there is a wide range of compositions where one can form quasicrystals + FCC Al.

Figures 3.21 and 3.22 are representative XRD data obtained from several different Al-Mn-Ce compositions, Al$_{91}$Mn$_{7}$Ce$_{2}$ [26], Al$_{92}$Mn$_{6}$Ce$_{2}$ [26], and Al$_{86}$Mn$_{12}$Ce$_{2}$ [24], along with binary Al$_{92}$Mn$_{8}$ [26] and Al$_{86}$Mn$_{14}$ [24] compositions as a reference. The XRD data shows that the materials consist mainly of the FCC Al + icosahedral phases with minor amounts of other equilibrium Al-Mn-Ce phases such as Al$_{6}$Mn, Al$_{10}$Mn$_{7}$Ce$_{2}$, and Al$_{8}$Ce. Here one can see that not only does the addition of Ce help in the formation of the icosahedral phase, but Ce also increases the icosahedral phase volume fraction. The addition of 2 at. % Ce for Mn in Al$_{92}$Mn$_{8}$ increases the volume fraction of the icosahedral phase as evident from the change in relative peak intensities observed in XRD data [26]. The volume fraction of the icosahedral phase determined from TEM micrographs was reported as 84%; although the authors due note that this might be slight over estimation. However, other studies have reported similar increases in volume fraction. For example, the substitution of 2 at. % Ce for Mn in an Al – 14 at. % Mn alloy
Figure 3.20: Plot of the Al-Mn-Ce compositions and the corresponding phase fields for solid solution of FCC Al, FCC Al + Quasicrystals, Quasicrystals + Amorphous, FCC Al + Amorphous, and Amorphous phases. The open and closed circles correspond to ductile or brittle bending behavior of the melt-spun ribbons. The value next to each data point corresponds to the crystallization temperature for each particular composition in Kelvin (K). Reproduced from ref [26].
Figure 3.21: Representative XRD data obtained from melt-spun specimens with compositions of Al$_{91}$Mn$_7$Ce$_2$, Al$_{92}$Mn$_6$Ce$_2$, and Al$_{92}$Mn$_8$. Peaks corresponding to the FCC Al and icosahedral phases are indexed. Reproduced from ref [26].
Melt-spinning experiments were performed with a wide variation of the process parameters. Depending on these conditions, ribbons with nonmetallic impurities of about 0.4 at.% Oxygen and about 0.02 at.% Nitrogen. Melt-spinning experiments were conducted as well. A Jeol JSM 6400 scanning electron microscope with 200 kV acceleration voltage and an energy dispersive X-ray spectroscopy (EDS) microanalysis were performed using a Jeol 2000FX analytical microscope. A dynamic testing system. In order to avoid effects of friction between the sample and the punches, the constant component of the load, the load was adjusted using an Instron 8562Fractometer with Co radiation (Perkin-Elmer DSC7) at a heating rate of 40 K/min was analyzed by differential scanning calorimetry (DSC) and an argon overpressure. Mechanical properties of the ingots were prepared by arc-melting pure metals. Therefore, the binary Al-Mn alloy was used.

![Figure 3.22: Representative XRD data obtained from melt-spun specimens with compositions of Al\textsubscript{86}Mn\textsubscript{14}, Al\textsubscript{86}Mn\textsubscript{12}Ce\textsubscript{2}, Al\textsubscript{92}Mn\textsubscript{6}Ce\textsubscript{2}, and Al\textsubscript{91}Mn\textsubscript{7}Fe\textsubscript{2}. Peaks corresponding to the FCC Al, icosahedral, and Al\textsubscript{6}Mn phases are indexed. Reproduced from ref [24].](image-url)
led to an increase in the volume fraction of the quasi-crystalline precipitates from 55% (Al$_{86}$Mn$_{14}$) to 80% (Al$_{86}$Mn$_{12}$Ce$_2$) [24]. Thus, suitable volume fractions of quasi-crystalline strengthening phases could be achieved at lower total solute contents, and at lower alloy densities, in Al-Mn-Ce alloys than in binary Al-Mn alloys. Quasi-crystal volume fractions of up to 70% have been reported in alloys with 4 – 6 at. % Mn and up to 3 at. % Ce [23-26, 99].

The microstructures obtained in these materials are broadly similar to those for single-phase quasicrystals. Figure 3.23(a) is a representative BF TEM image obtained from a melt spun Al$_92$Mn$_6$Ce$_2$ alloy. The dark particles is the quasicrystalline phase, while the bright regions in-between the particles is the FCC Al phase. As in the single-phase materials, the quasicrystalline phase exhibits an equiaxed morphology with a grain size reported between 50 and 100 nm [24]. The FCC Al phase consists of a thin film surrounding all of the quasicrystalline particles with a thickness between 5 and 15 nm [24]. Figures 3.23(b)-(d) are representative SADPs obtained from the quasicrystalline particles, which exhibit the characteristic five-, three-, and two-fold symmetry patterns expected from an icosahedral phase. [24]. Furthermore, DSC experiments carried out on many of these materials show that these microstructures are very stable, with crystallization temperatures as high as 720 K. This raises the possibility of using these types of materials in applications subject to elevated temperature.

3.3.2 *Mechanical Properties*

These Al-rich alloys exhibit much higher strengths than those achievable in commercially available Al alloys. Using the same phase field plot shown in Figure 3.20,
Figure 3.23: Representative (a) BF TEM image and corresponding SADPs along the (b) five- (c) three- and (d) two-fold axes obtained from a melt-spun Al\textsubscript{0.2}Mn\textsubscript{6}Ce\textsubscript{2} alloy. Reproduced from ref [24].
Inoue et al presented the tensile fracture strengths measured in several different Al-Mn-Ce alloys produced by melt spinning in Figure 3.24. The value next to each of the data points is the measured tensile fracture strength from the as-spun ribbon. The materials were categorized into two groups, ductile or brittle, which are denoted either by an open or filled circle, respectively. These two descriptions refer to the behavior observed when the ribbons were bent by 180°. If the specimen did not exhibit any cracking after bending then it was categorized to be ductile, while the materials that cracked or fractured with bending were sorted at brittle. Here one can see that tensile fracture strengths measured for the materials consisting of FCC Al + quasicrystals were as high as 1320 MPa [26]. This strength value is more than twice that achievable in peak aged-hardened Al alloys. The hardness of these kinds materials are also higher than conventional Al alloys with values reported greater than 400 VHN [22, 26].

However, many studies opted not to measure the tensile strength of these materials for two reasons: 1) For melt spun ribbons, there is a considerable amount of difficulty in reliably measuring the cross section of the fractured ribbons and 2) performing the actual tensile test is rather difficult due to the inherently small geometry; for melt spun ribbons, many of the specimens fail at the grips of the apparatus; for specimens that are cast into rods, the geometry is not sufficient to allow the machining of a tensile specimen. As such, some of the other strength measurements are performed under compressive loads. Schrack et al conducted a series of compression strength tests on squeeze cast rods produced with diameters of approximately 5 mm. The specimens were loaded until they fractured. Figure 3.25 is a plot of several stress/strain curves obtained from specimens with compositions of Al\textsubscript{90}Mn\textsubscript{8}Ce\textsubscript{2} and Al\textsubscript{92}Mn\textsubscript{6}Ce\textsubscript{2}. The
Figure 3.24: Plot of the Al-Mn-Ce compositions and the corresponding phase fields for solid solution of FCC Al, FCC Al + Quasicrystals, Quasicrystals + Amorphous, FCC Al + Amorphous, and Amorphous phases. The open and closed circles correspond to ductile or brittle bending behavior of the melt-spun ribbons. The value next to each data point corresponds to the tensile fracture strength for each particular composition in MPa. Reproduced from ref [26].
Al₉₀Mn₈Ce₂ alloy, which has a higher volume fraction of quasi-crystals, exhibited the highest strength with a value of 830 MPa, but this composition exhibited the lowest strain to failure of 1%. The Al₉₂Mn₆Ce₂ exhibited a much lower value in strength (565 MPa), but exhibited much better ductility with a strain to failure of 13.6%.

In terms in deformability, it has been reported that these materials do exhibit good cold workability. Also, it is important to note that there is some evidence of work softening like in single-phase quasicrystals. Inoue et al reported tensile fracture strength and hardness values measured for a melt spun Al₉₂Mn₆Ce₂ alloy in the as-quenched condition and after cold rolling [18]. Figure 3.26 is a plot of the tensile fracture strength and Vickers hardness versus cold rolling area reduction. Here one can see that the strength and hardness decrease with increased cold rolling. This phenomenon has been attributed to the increased interface area produced by the fracturing of the quasicrystals into smaller particles. These interfaces then act as dislocations sinks, thus reducing the strain hardening effect.

As mentioned above, these microstructures exhibit excellent thermal stability at elevated temperature. In addition, the mechanical properties at elevated temperature are also vastly superior to those achievable in conventional Al alloys. The yield strength, fracture strength and strain to failure measured from compression tests performed on squeeze cast rods of Al₉₀Mn₈Ce₂ at various elevated temperatures are shown in Figure 3.27. As one would expect, the yield and fracture strength both decrease with increasing temperature and vice versa for the strain to failure. However, note that the decrease is very gradual, where at homologous temperatures of 0.6, the strength values are 50% of
Figure 3.25: Plot of the stress/strain curves measured in compression from squeeze cast rods of Al$_{90}$Mn$_8$Ce$_2$, Al$_{92}$Mn$_6$Ce$_2$, and Al$_{91}$Mn$_7$Fe$_2$, and consolidated Al$_{94}$Mn$_3$CrCu$_2$ powder. Reproduced from ref [24].
Figure 3.26: Plot of tensile fracture strength and Vickers hardness versus cold rolling reduction in area (%) of melt-spun specimens of $\text{Al}_{92}\text{Mn}_6\text{Ce}_2$ and $\text{Al}_{94.5}\text{Cr}_3\text{Ce}_1\text{Co}_{1.5}$. Reproduced from ref [18].
Figure 3.27: Plot of the fracture strength, yield strength, and strain to failure measured in compression versus testing temperature for an Al_{90}Mn_{8}Ce_{2} alloy. Reproduced from ref [24].
the room temperature values. This is a vast improvement over conventional Al alloys, where the strength drastically drops at these sorts of temperatures.

There has been some work performed on quasicrystalline alloys produced by the consolidation of atomized powders by warm extrusion [18]. The gas-atomized process provides the sufficient cooling rates necessary to produce these metastable phases, and the material is carefully consolidated below the crystallization temperature. The result is bulk materials with microstructures consisting of FCC Al + quasicrystals. A summary of the mechanical properties exhibited by these materials is presented in Figure 3.28, along with data points corresponding to those for conventional Al alloys. It is clear that these icosahedral alloys offer vast improvements in strength over conventional Al alloys by at least a factor of two. Thus, these types of materials can form the basis for new high-strength low-density Al based alloys for use in weight sensitive applications.
Figure 3.28: Plot of the tensile fracture strength versus elongation to failure for various icosahedral-based materials produced by consolidation of gas-atomized powder and different conventional Al-based alloys. Reproduced from ref [18].
Chapter 4: Materials and Experimental Methods

4.1 Materials

4.2 Experimental Methods and Characterization

4.2.1 Vickers Hardness

4.2.2 X-Ray Diffraction (XRD)

4.2.3 Scanning Electron Microscopy (SEM)

4.2.4 Transmission Electron Microscopy (TEM)
Chapter 4: Materials and Experimental Methods

For this study, x-ray diffraction and electron microscopy techniques were used to characterize the microstructural changes that occurred after heat treatment of the as-extruded material at various temperatures and times.

4.1 Materials

The gas turbine engine company, Pratt & Whitney, provided the Al alloys used in this study, which had compositions of Al-3.71Ni-0.44Co-0.17Zr-2.95Y and Al-4.81Mn-2.0Ce (all in at. %). Powder metallurgy techniques were used in the production of these alloys. A schematic diagram of the sequence of processing techniques used to produce these alloys is shown in Figure 4.1. First, a master alloy with the appropriate composition was produced by vacuum induction melting at Great Western Technologies and cast into ingots. Gas atomized powder was produced from the master alloy at Valiment Company by melting the ingots under argon cover in a vacuum furnace which lies above the atomization chamber. The melt was then gravity-fed through a nozzle equipped with high pressure helium gas jets. The high-pressure jets of gas forced the liquid metal stream to break up into small droplets that cooled rapidly into powder particles. The cooling rates achieved in gas atomization can be high enough to form the metastable phases used in these alloys. The particles fall and are collected at the bottom of the chamber. The powder particles were then canned at DWA Aluminum Composites by sieving the Valimet powder to -450 mesh (32 µm), placing the sieved powder into 25 cm diameter CP Al extrusion cans, statically degassing the powder by evacuating the cans to \( \approx 10^{-6} \) torr, and then sealing the evacuated cans. The canned billets were ram
Figure 4.1: Schematic of the sequence of processing techniques used to produce the Al-Ni-Co-Zr-Y alloy. (a) Gas atomization of master alloy into amorphous powders. (b) Powders compacted and sealed into Al cans. (c) Cans are then ram extruded at high pressure and temperature to consolidate and devitrify the amorphous powders. (d) Bar is cut perpendicular to the extrusion direction into smaller sections.
extruded at H. C. Starck in a 4500 tonne press; the billets were preheated to ≈310°C and then extruded to a diameter of 7.2 cm (a 12:1 extrusion ratio). The extruded ingots were then decanned, and coupons were cut from the decanned extrudate for heat-treatment experiments. Coupons were heat-treated in laboratory air using a furnace at temperatures of 300, 350, 400, 450, 475 and 500 °C for times of 2, 8, 24, 48 and 96 h and then quenched using water.

4.2  Experimental Methods and Characterization

4.2.1  Vickers Hardness

The effects of heat treatment on mechanical behavior were evaluated by measuring the Vickers micro-hardness. Samples for hardness measurements were prepared using standard metallographic techniques. Thin slices were cut through the coupons perpendicular to the extrusion direction of the material. These slices were ground mechanically using successively finer grades of SiC grinding paper starting with 240 grit and working down to 1200 grit using only distilled water as a lubricant. Final polishing was performed using a 0.3 μm Alumina suspension or a 0.5 μm Colloidal Silica suspension. Hardness measurements were obtained using a 200g load in the center of polished sections to avoid any effects from surface oxidation. The size of the hardness indents were large enough to sample a sufficiently large number of microstructural features; thus giving a representative value of the samples’ bulk hardness.
4.2.2  *X-Ray Diffraction (XRD)*

X-Ray Diffraction (XRD) data were collected from samples of the as-atomized powder, from the as-extruded material, and from sections through the heat-treated coupons. The data were acquired in Bragg-Brentano geometry using a Siemens D500 diffractometer equipped with a curved graphite monochromator and a Bruker D2 Phaser, both using Cu Kα radiation. The XRD measurements were performed with a scan step of 0.016 degrees over a 2θ range of 10 to 95 degrees. Phase identification was performed using the PANalytical software X’Pert High Score Plus with the ICDD PDF4 database and standard JCPDS files in EVA. Phase volume fractions were determined by Rietveld analysis after correction for any crystallographic texture effects using the March-Dollase model. Since there is no JCPDS standard for the Al$_{19}$Ni$_5$Y$_3$ phase, the peaks were indexed as follows. Firstly, the software package Crystal Maker and Crystal Diffract were used to tabulate the d-spacings expected from an orthorhombic Al$_{19}$Ni$_5$Y$_3$ crystal with the structure defined by Vasiliev et al [29]. These were then compared to the peaks observed in the spectrum apart from those belonging to FCC Al and labeled accordingly.

4.2.3  *Scanning Electron Microscopy (SEM)*

The samples prepared for Vickers micro-hardness were also used for scanning electron microscopy. SEM images were acquired using the electron column on a FEI Dual Beam Strata 400S system, which has a Schottky field emission gun, and a JEOL JSM 6330F FESEM, which has a cold cathode field emission gun. Both instruments were operated at an accelerating voltage of 3 kV for optimum resolution. The detector used on the FEI Dual Beam Strata 400S system was the high-resolution through-the-lens...
detector (TLD) in either free-field or immersion mode, while an Everhart-Thornley (ETD) detector was used on the JEOL JSM 6330F FESEM. Both secondary electron (SE) and backscattered electron (BSE) images were obtained using these instruments.

4.2.4 Transmission Electron Microscopy (TEM)

TEM samples were prepared by cutting thin slices of material perpendicular to the extrusion direction. These slices were further thinned by mechanically grinding to below 0.1 mm in thickness. A disk punch was then used to extract 3 mm diameter disks from these thin sheets. The disks were thinned to perforation in a Struers Tenupol-5 twin jet electropolisher using an electrolyte consisting of 90% Methanol, 10% Perchloric Acid at approximately -20°C and 20 V. Some of the foils required further thinning by Ar ion milling to eliminate differential electropolishing effects; this was accomplished in a Gatan model 600 Duomill at an accelerating voltage of 3 kV using liquid nitrogen cooling to minimize ion beam damage.

TEM analysis was performed using a FEI T12 Tecnai S/TEM operated at 120 kV. This instrument is equipped with an ultra-thin window EDAX energy dispersive X-ray spectrometer (EDXS). For higher resolution analysis a JEOL JEM-2010 TEM was used operating at 200 kV. This microscope is equipped with a UHR objective lens polepiece ($C_s \approx 0.5$ mm), which gives a point-to-point resolution of $<0.19$ nm at Scherzer defocus, and an EDAX Phoenix EDXS detector that has a super-ultrathin polymer window.

Zone axis selected area diffraction patterns (SADPs) obtained in the TEMs were indexed by comparison with patterns calculated using the software package SingleCrystal
(CrystalMaker Software Ltd.) with published values of the lattice parameters and atomic positions for the appropriate phases.
Chapter 5: Al-Ni-Co-Zr-Y Alloy

5.1 Results

5.1.1 Starting Microstructure

5.1.2 Effect of Heat-Treatment on Hardness

5.1.3 Effect of Heat-Treatment on Phase Stability

5.1.4 Coarsening of the 19-5-3 Phase

5.1.5 Grain Growth in the FCC Al Phase

5.2 Discussion

5.2.1 Overall Microstructure and Hardness

5.2.2 Coarsening of the Microstructure

5.3 Conclusions
Chapter 5: Al-Ni-Co-Zr-Y Alloy

The following chapter contains the results, discussion and conclusions sections pertaining to the work performed on the Al-3.71Ni-0.44Co-0.17Zr-2.95Y (at.%) alloy.

5.1 Results

5.1.1 Starting Microstructure

The phases present in the as-extruded material were first identified by XRD; Figure 5.1 is a representative XRD scan obtained from a section cut perpendicular to the extrusion direction. Four of the most intense peaks correspond to the \{111\}, \{200\}, \{220\} and \{311\} planes expected for FCC Al with a lattice parameter $a_0 = 0.405$ nm. All of the remaining peaks correspond to those expected for the orthorhombic 19-5-3 compound identified by Vasiliev et al [29] ($a_0 = 0.403$ nm, $b_0 = 1.589$ nm, $c_0 = 2.689$ nm). For simplicity, indices are provided for only the most intense 19-5-3 peaks on Figure 5.1. There was no evidence from the XRD data of any Al$_3$X binary phase in the as-extruded material.

SEM and TEM techniques were used to investigate the distribution and morphology of the phases present in the as-extruded material. Figure 5.2a is a representative secondary electron (SE) SEM micrograph obtained from a section cut perpendicular to the extrusion direction. The large differences in atomic density and bonding between the two phases present in the material leads to the high levels of contrast observed in these images. The dark background corresponds to the FCC Al matrix, while the bright, rod- and ellipsoidal-shaped features correspond to the intermetallic particles. Although the distribution of the 19-5-3 phase appears to vary
Figure 5.1: XRD data obtained from the as-extruded material. The four strongest peaks for the FCC Al phase and the 9 strongest peaks from the 19-5-3 phase are indexed.
significantly from one location to another, measurements from several such images gave consistent values of \( \approx 22\% \) for the mean volume fraction of the intermetallic. The morphologies and sizes of the phases were revealed more clearly by TEM. A representative bright field (BF) TEM micrograph of the as-extruded microstructure is presented in Figure 5.2b; in this image, the electron beam direction lies parallel to the extrusion axis. A combination of mass-thickness and diffraction contrast causes the intermetallic particles to appear dark, while the surrounding FCC Al matrix appears much brighter. A higher magnification BF TEM image of a selected intermetallic particle together with the corresponding [100] zone axis selected area diffraction pattern (SADP) and a calculated pattern are shown in Figure 5.2c. All of the SADPs obtained from these dark particles are consistent with those expected for the orthorhombic 19-5-3 crystal structure, and in most cases the beam direction lay close to [100]_{19-5-3}. This is consistent with our previous studies of devitrified Al-Ni-Y alloys in the as-extruded condition wherein the 19-5-3 phase adopted a plate-like morphology with the major axis [100]_{19-5-3} parallel to the extrusion axis [27-35]. Thus, in sections cut perpendicular to this axis the particles appear as short rods with the plate thickness parallel to [001]_{19-5-3} and the plate width parallel to [010]_{19-5-3}. Occasional equiaxed particles with diameters of 30 nm or less were also observed in the microstructure. Chemical microanalysis (not shown) revealed that these small particles are enriched in Y and Zr. Although these particles are too small to obtain suitable diffraction patterns to determine the exact phase and crystal structure, the EDXS data suggest that they may be initial precipitates of the binary intermetallic phase(s) expected in this material.
Figure 5.2: Representative micrographs showing the overall microstructure of the as-extruded material viewed parallel to the extrusion direction: (a) SE SEM, (b) BF TEM, and (c) higher magnification BF TEM of an edge-on plate with the corresponding [100] zone axis SADP and a calculated [100] zone axis pattern for the 19-5-3 structure.
5.1.2 Effect of Heat-Treatment on Hardness

Vickers micro-hardness testing was performed on the as-extruded and heat-treated materials. A plot of the Vickers hardness number (VHN) versus heat-treatment time for materials heat-treated at 300, 350, 400, 450, 475 and 500 °C for times of 2, 8, 24, 48 and 96 h is presented in Figure 5.3. Each point on the plot is the average of 5 hardness values. For clarity, errors bars are not shown on the plot, because they would be obscured by the data point symbols in most cases; we note that the maximum variability observed (± one standard deviation) for the extrudate and materials heat-treated at 300, 350, 400, 450, 475 and 500°C was 1.5, 2.4, 2.4, 1.5, 1.3, 2.2 and 1.2 VHN, respectively. The hardness of the as-extruded material was 163 VHN, as denoted by the point at 0 h. For the material heat-treated at 300°C, there is a slight increase in hardness after 2 h to a value of 168 VHN. However, with further heat-treatment the material exhibits a gradual decrease in hardness, reaching a value of 157 VHN after 96 h. For the 350°C heat-treatment, the material exhibits a steady decrease in hardness with heat-treatment time reaching a value of 149 VHN after 96 h. For the samples heat-treated at 400, 450, 475 and 500°C, there is an initial rapid decline in hardness over the first 2 h to 146, 136, 127 and 122 VHN, respectively followed by a more gradual softening to 135, 122, 116 and 95 VHN, respectively after 96 h.

5.1.3 Effect of Heat-Treatment on Phase Stability

The origins of the change in the mechanical response upon heat treatment were first investigated using XRD to determine if this might be a result of changes in the phases present. The XRD data obtained over the 2θ range of 20-80° from the samples
Figure 5.3: Mean values of the Vickers micro-hardness data from the as-extruded material (denoted by black square at 0 h) and the materials heat-treated at 300-500 °C for 2, 8, 24, 48 and 96 h. The lines through these data points for each heat-treatment temperature are intended as a guide for the eye. Error bars are not shown, but in each case the standard deviation is less than 2.5 VHN.
heat treated at 300-500°C for 96 h showed no significant changes in the positions or intensities of the intermetallic phase peaks from those shown in Figure 5.1. In higher resolution scans from these samples over the 2θ range of 23-36°, a few additional peaks were observed as shown in Figure 5.4. There are no peaks from the FCC Al matrix since these all lay at higher angles (2θ > 38°) and all of the peaks for the as-extruded and 300°C samples correspond to those expected for the 19-5-3 phase. For samples heat-treated at 350°C and above, however, there are four additional peaks at 2θ = 23.83°, 27.05°, 29.07° and 33.95°. The intensities of these peaks increase, and the full width at half maximum values decrease, as the heat treatment temperature rises. The positions of these peaks are close to those expected for the {10\overline{1}4}, {01\overline{1}5}, {11\overline{2}0} and {02\overline{2}1} planes of Al₃Y with the rhombohedral Pb₃Ba structure phase, although the measured lattice parameters (a₀ = 0.6142 nm, c₀ = 2.084 nm) differ somewhat from published values (a₀ = 0.6204 nm, c₀ = 2.1184 nm [100]). We note that the only other strong peak expected for the rhombohedral Al₃Y phase in this angular range is that from the {20\overline{2}2}, but the position of this peak coincides with that from the {048} of the 19-5-3 phase.

Although there is no XRD evidence for the presence of Al₃Y in the extrudate and in the sample heat-treated at 300°C for 96 hours, fine particles enriched in Y and/or Zr were detected in these samples by TEM. These particles are presumably the early stages of precipitation of other intermetallic phases, but the sizes of these particles are so small and the volume fractions are so low that they do not give detectable peaks in the XRD scans. Coarser Al₃(Y,Zr) intermetallic particles were detected by TEM in the samples heat-treated for 96 h at higher temperatures. Representative examples of BF TEM images with corresponding SADPs obtained from Al₃(Y,Zr) particles in the sample heat-treated
Figure 5.4: XRD data obtained over a 2θ range of 23-36° from the as-extruded material and from samples heat-treated at 300-500 °C for 96 h. The top row of indices corresponds to the strongest peaks from the 19-5-3 phase (shown in red), and the bottom row of indices corresponds to the four peaks arising from the rhombohedral Al₃Y phase (shown in black).
at 500°C are shown in Figure 5.5. The particle in Figure 5.5(a) is Y-rich and the SADP corresponds to the [2\overline{2}01] zone axis for the rhombohedral Ba₃Pb-type polymorph of Al₃Y, which is consistent with the XRD data from this sample. Such particles contained up to 2 at.% Zr, were equi-axed, and had diameters of up to 2.5 µm. It is presumably the substitution of Zr into the Al₃Y that is responsible for the difference between the published lattice parameters and those measured here by XRD (Figure 5.4). The particle in Figure 5.5(b) is Zr-rich and the SADP corresponds to the [010] zone axis for the D0₂₃ polymorph of Al₃Zr. These particles adopted a polyhedral morphology with a maximum diameter of 300 nm and contained up to 4 at.% Y. No XRD peaks corresponding to this latter phase were observed for any of the samples considered in this study, presumably because the volume fractions are too low to give a detectable signal.

Since the volume fractions of the Al₃(Y,Zr) phases were so low (< 3% by volume even after 96 h at 500°C based upon SEM and TEM data), they are unlikely to have a significant effect upon the mechanical response of the samples. As such, only the microstructural development of the 19-5-3 and the FCC Al phases was considered further.

### 5.1.4 Coarsening of the 19-5-3 Phase

The coarsening of the 19-5-3 phase was evaluated using SE SEM micrographs obtained from sections cut perpendicular to the extrusion direction (i.e. similar to Figure 5.2a). Since the 19-5-3 plates tend to be oriented parallel to the extrusion direction, they appear as rods in cross-section, and we refer to the major and minor axes in the plane of the section as the width and thickness of the plate, respectively. Representative SE SEM
Figure 5.5: Representative BF TEM images, zone axis SADPs and calculated patterns for examples of Al$_3$(Y,Zr) phases in the sample heat-treated at 500 °C for 96 h: (a) rhombohedral Al$_3$Y with \( \mathbf{B} = [2\bar{2}01] \); (b) tetragonal Al$_3$Zr with \( \mathbf{B} = [010] \).
images from the samples heat-treated at 300, 350, 400, 450, 475 and 500 °C for 2 – 96 h are presented in Figures 5.6 – 11, respectively. The SE SEM images presented for the samples heat-treated at 300 – 450 °C (Figures 5.6 – 9) were obtained at the same magnification, while the images obtained for the 475 and 500 °C heat-treatments (Figures 5.10 & 11, respectively) were obtained at a much lower magnification to better show the distribution and extent of growth for the 19-5-3 phase at those temperatures.

The width and thickness of the 19-5-3 plates were measured using SE SEM images like those presented in Figures 5.2a and 5.6 – 9 for the as-extruded material and samples heat-treated at 300 – 500 °C, respectively. Distributions of the 19-5-3 particle dimensions measured from the as-extruded material and samples heat-treated at 300, 350, 400, 450, 475 and 500 °C are presented in Figures 5.12 – 5.18, respectively for times of 2, 8, 24, 48 and 96 h. Each histogram represents at least 200 measurements. The width and thickness distributions are plotted up to 600 and 200 nm using 25 and 10 nm bins, respectively with an extra bin at the end for dimensions exceeding 600 and 200 nm. For heat treatments at below 450°C the distributions are essentially mono-modal with the distributions becoming broader and the peak shifting slowly to higher mean values with extended exposure. At the higher temperatures, however, there is a rapid transition to a bimodal size distribution with the numbers of small particles falling and large particles rising with increasing time.

The overall trends in the coarsening of the 19-5-3 plates are perhaps more clearly shown Figures 5.19(a)-(f), which are plots of the mean values of the width and thickness against heat-treatment time from the samples heat-treated at 300 – 500 °C, respectively. In each case the values at 0 h represent those for the as-extruded material. Each width and
Figure 5.6: SE SEM Images obtained from the sample heat-treated at 300 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.7: SE SEM Images obtained from the sample heat-treated at 350 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.8: SE SEM Images obtained from the sample heat-treated at 400 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.9: SE SEM Images obtained from the sample heat-treated at 450 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.10: SE SEM Images obtained from the sample heat-treated at 475 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.11: SE SEM Images obtained from the sample heat-treated at 500 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.12: Distributions of particle dimensions in the as-extruded sample.
Figure 5.13: Distributions of particle dimensions in the samples heat-treated at 300 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.14: Distributions of particle dimensions in the samples heat-treated at 350 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.15: Distributions of particle dimensions in the samples heat-treated at 400 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.16: Distributions of particle dimensions in the samples heat-treated at 450 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.17: Distributions of particle dimensions in the samples heat-treated at 475 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
Figure 5.18: Distributions of particle dimensions in the samples heat-treated at 500 °C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h.
thickness value is the arithmetic mean of at least 200 individual measurements, and error bars are not shown, but the variability can be seen from the particle size distributions in Figures 5.12 – 18. It is clear that the 19-5-3 plates coarsen very slowly at 300, 350, 400, and 450 °C, but much more quickly at 475 and 500 °C. The width and thickness increase from 204 and 64 nm in the extrudate to 245 and 71 nm after 96 h at 300 °C, 255 and 81 nm after 96 h at 350 °C, 300 and 84 nm after 96 h at 400°C, 375 and 112 nm after 96 h at 450 °C, 790 and 157 nm after 96 h at 475 °C, and 1690 and 300 nm after 96 h at 500°C. From the SE SEM images and the particle size distributions it is clear that the more rapid coarsening at the higher temperatures corresponds to the development of a secondary population of much larger 19-5-3 particles with widths of up to 10 µm and thicknesses of up to 1 µm. The SE SEM images show that these large 19-5-3 particles start to appear after a short time at 475 or 500°C; the number of these particles increases as the population of smaller particles is depleted with increasing heat-treatment time.

The overall trend in coarsening of the 19-5-3 phase with heat-treatment temperature is shown in Figure 5.20, which is a plot of mean 19-5-3 plate width and thickness against heat-treatment temperature in the samples heat-treated for 96 h. Here it can be seen that the width and thickness after 96 h increase slowly from 245 and 71 nm at 300°C to 345 and 110 nm at 450°C; thereafter, the corresponding dimensions increase rapidly to 790 and 157 nm at 475°C and 1690 and 300 nm at 500°C.

5.1.5 *Grain Growth in the FCC Al Phase*

Due to weak orientation contrast in the SEM images, BF TEM imaging was used to investigate the variation of the Al grain size in the samples heat-treated for 96 h. For
Figure 5.19: Plots of the mean 19-5-3 particle widths and thicknesses against heat-treatment time measured from samples heat-treated at: (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 475°C and (f) 500 °C. Error bars are not shown, but full particle size distributions for these samples are shown in Figures 12-18.
Figure 5.19: Plots of the mean 19-5-3 particle widths and thicknesses against heat-treatment time measured from samples heat-treated at: (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 475°C and (f) 500 °C. Error bars are not shown, but full particle size distributions for these samples are shown in Figures 12-18.
Figure 5.19: Plots of the mean 19-5-3 particle widths and thicknesses against heat-treatment time measured from samples heat-treated at: (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 475°C and (f) 500 °C. Error bars are not shown, but full particle size distributions for these samples are shown in Figures 5.12-18.
Figure 5.20: Plot of the mean 19-5-3 particle widths and thicknesses against heat-treatment temperature measured from samples heat-treated for 96 h. Error bars are not shown, but full particle size distributions for these samples are shown in Figures 5.13(e)-18(e).
each area of interest, several BF images were acquired at slightly different sample orientations. Only the grains that gave strong diffraction contrast, and whose boundaries could thus be defined unambiguously, were measured. Representative examples of BF TEM images from the as-extruded material and samples heat-treated for 96 h at 300, 350, 400, 450, 475 and 500°C are shown in Figures 5.21(a), (b), (c), (d), (e), (f) and (g), respectively. We note that in many cases the boundaries of the Al grains are decorated heavily with 19-5-3 plates, indicating that these grains will be pinned strongly.

Distributions of the Al grain size measured from the as-extruded material and from samples heat-treated at 300, 350, 400, 450, 475 and 500°C for 96 hours using BF TEM images like those shown in Figure 5.21 are presented in Figures 5.22(a) – (g), respectively. Each histogram represents at least 100 measurements. The grain size distributions are plotted up to 2 µm using 50 nm bins with an extra bin at the end for grain diameters exceeding 2 µm. For heat-treatments at below 450 °C, the distributions are essentially mono-modal becoming slightly broader and with the peak shifting slowly to higher mean values with increasing heat-treatment temperature. For the material heat-treated at 475 °C, the distribution peak exhibits a more drastic shift towards higher grain size values. At 500 °C, the distribution has become very broad and the appearance of a bimodal size distribution has occurred.

The trends in the Al grain growth are revealed more clearly in Figure 5.23, which is a plot of mean grain size against heat treatment temperature for all the 96 h samples; each data point represents the arithmetic mean of over 100 measurements. The grain size after 96 h rises steadily from 420 nm at 300 °C to 708 nm at 450 °C. At higher
Figure 5.21: Representative bright field TEM images obtained from the (a) as-extruded material and samples heat-treated for 96 h at: (b) 300°C, (c) 350°C, (d) 400°C, (e) 450°C, (f) 475°C and (g) 500°C.
Figure 5.22: Distributions of Al grain size for the (a) as-extruded material and samples heat-treated for 96 h at: (b) 300°C, (c) 350°C, (d) 400°C, (e) 450°C, (f) 475°C and (g) 500°C.
Figure 5.23: Plot of the mean values of the Al grain size against heat-treatment temperature measured from samples heat-treated for 96 h. Error bars are not shown, but full grain size distributions for these samples are shown in Figure 5.22.
temperatures the grain growth is more extensive with final grain sizes of 950 and 1300 nm at 475 and 500 °C, respectively.

5.2 Discussion

5.2.1 Overall Microstructure and Hardness

The phases present in the as-extruded material are consistent with those observed previously in similar Al-Ni-Y based alloys studied by our group [27-35]. The extrudate exhibits a two-phase microstructure with a FCC Al matrix and 22% by volume of plate-like intermetallic particles adopting the Al$_{19}$Ni$_3$Gd$_3$-type crystal structure [68]. This 19-5-3 phase is retained at approximately the same volume fraction in samples heat-treated at temperatures of up to 500°C for up to 96 h. This is consistent with our previous conclusion that the 19-5-3 phase is the equilibrium ternary phase in Al-rich Al-Ni-Y-based alloys [27, 29], despite the fact that this phase is dismissed as “probably metastable” in a recent re-evaluation of the Al-Ni-Y system by Raghavan [101]. The only phase changes that occur upon heat-treatment are the development of up to 3% by volume of Al$_3$(Y,Zr) phases. These are a mixture of Al$_3$Y with the Ba$_3$Pb structure plus a little Al$_3$Zr with the D0$_{23}$ structure. For these crystal structures the phase volume fractions that one would expect in an alloy with this composition are 73.4% FCC Al, 21.1% Al$_{19}$(Ni,Co)$_3$Y$_3$, 2.1% Al$_3$Y and 3.4% Al$_3$Zr. While the observed volume fractions of the Al, 19-5-3 and Al$_3$Y phases are broadly consistent with these values, there is far less Al$_3$Zr. This is presumably due to significant solubility of Zr in the other phases. Since the mechanical response of the alloy will be dominated by the distribution of the majority
FCC Al and 19-5-3 phases, the effects of the Al₃Y and Al₃Zr phases are not considered further in the remainder of this discussion.

The hardness data presented in Figure 5.3 show that this alloy is remarkably resistant to softening. The hardness decreases by about 4% and 17% after 96 h at 300 and 400 °C, respectively. This softening is far less than one would expect for conventional high-strength Al alloys at these temperatures. We have suggested previously [27] that such systems behave more like short-fiber- or particle-reinforced composites with strong interfacial bonding than precipitation- or dispersion-hardened alloy. Attempts were made to relate the measured hardness to the majority phase dimensions. The relationships between the hardness and the majority phase dimensions (Al grain size and 19-5-3 plate width and thickness) are shown in Figure 5.24. In Figure 5.24(a) the mean width and thickness of the 19-5-3 phase, and the mean diameter of the Al grains, for the extrudate and for all 30 heat-treated samples are plotted against the mean value of the hardness for the corresponding samples. Figures 5.24 (b) and (c) are the same data with the reciprocal and the square root of the reciprocal phase dimensions on the abscissae, respectively. In Figure 5.24(a), there appears to be a strong linear variation in hardness with the phase dimension down to hardness values of 120 VHN, corresponding to the samples heat-treated at temperatures of up to 450°C. However, this is just an artifact of plotting all three curves using the same scale on the abscissae. If one were to plot all three curve separately using appropriate scales, then one could see the scatter in the data more clearly, where the quantitative measures of linear fit (i.e. R²) are 0.786 for the width/thickness and 0.993 for the grain size. If one were to use all of the data points in Figure 5.24(a) the R² values for the width/thickness and grain size drop to 0.579 and
Figure 5.24: Plots of the mean values of hardness against: (a) mean values of 19-5-3 plate width and thickness, and Al grain size; (b) the reciprocals of these values; (c) the reciprocals of the square roots of these values. Error bars are omitted for clarity.
Figure 5.24: Plots of the mean values of hardness against: (a) mean values of 19-5-3 plate width and thickness, and Al grain size; (b) the reciprocals of these values; (c) the reciprocals of the square roots of these values. Error bars are omitted for clarity.
0.931, respectively. Given that the volume fraction of the 19-5-3 phase is constant at 22%, the mean inter-particle separation, \( \lambda \), would be proportional to the particle width or thickness, assuming a fixed particle aspect ratio. Thus, if the observed variation of hardness were due to Orowan looping, one would expect the strength to be proportional to \( \lambda^{-1} \). However, the linear fit for the hardness data plotted against \( \lambda^{-1} \) (Figure 5.24(b)) and \( \lambda^{1/2} \) (Figure 5.24(c)) are not significantly different than those obtained from 5.25(a) with \( R^2 \) values of 0.861 and 0.990 for the width/thickness and grain size, respectively. The best linear fit to the grain size data is given by \( d^{-1/2} \) (Figure 5.24(c)), as one might expect for Hall-Petch type grain-size strengthening, but we note that similar values of correlation coefficient were obtained for \( d \) and \( d^{-1} \) in Figures 5.24(a) and 5.24(b), respectively. Due to the ambiguity in the data it was not possible to distinguish between possible deformation micro-mechanisms on this basis.

For Al-RE-TM alloys of the type considered in this study, the gas-atomized powders are at least partially amorphous [33]. The fully crystalline microstructure in the extrudate develops by devitrification of the amorphous material during pre-heating of the canned powder and/or during extrusion due to adiabatic heating effects. This process leads to a distribution of 19-5-3 phase plates, each of which is surrounded by several Al grains. As such, these 19-5-3 plates are not precipitates within the FCC Al and there is no well-defined orientation relationship between the two phases. Thus, the distinct morphology of the 19-5-3 plates is presumably a manifestation of pronounced surface energy anisotropy in this complex orthorhombic crystal structure. The strong axial texture in the 19-5-3 phase is a geometric result of the plates rotating during extrusion to align with the direction of metal flow [27]. Once the extrudate microstructure has been
established, any subsequent changes in the mechanical response upon heat treatment must correspond to changes in the dispersion of the 19-5-3 phase and/or the grain size of the FCC Al phase. These processes are considered in more detail below.

5.2.2 Coarsening of the Microstructure

We consider first the coarsening of the 19-5-3 phase with heat-treatment. The kinetics of diffusion-controlled coarsening of particles usually takes the general form:

\[ \bar{x}_t^n - \bar{x}_i^n = kt \]

where: \( \bar{x}_t \) is the mean particle size at a time \( t \), \( \bar{x}_i \) is the initial mean particle size, \( n \) is the coarsening exponent and \( k \) is a growth constant. The measurements of mean plate width and thickness obtained from the 19-5-3 phase in the heat-treated samples were analyzed by plotting \( \bar{x}_t^n - \bar{x}_i^n \) against \( t \) at each heat-treatment temperature for various values of \( n \). The best fit to the data was obtained for \( n = 3 \), corresponding to Ostwald-type ripening of the plates. The plots of \( \bar{x}_t^3 - \bar{x}_i^3 \) against \( t \) for the mean plate widths and thicknesses are shown in Figures 5.25-30. Activation energies for the ripening process were obtained by fitting the temperature dependence of \( k \) to an Arrhenius relationship:

\[ k = k_0 \exp(-Q/RT) \]

where: \( k_0 \) is a constant, \( Q \) is the activation energy, \( R \) is the gas constant and \( T \) is the temperature. The resultant log \( k \) versus \( 1/T \) plots for the width and thickness data are shown in Figure 5.31. Both plots show two linear regimes with distinctly different slopes corresponding to the samples heat-treated at 300-400°C and 450-500°C. For the lower temperature heat-treatments, the values of \( Q \) obtained from the mean width and thickness data are 16.0 and 14.3 kJ/mol, respectively while the values determined from the higher
Figure 5.25: Kinetics plots for the 19-5-3 plate (a) widths and (b) thicknesses in the sample heat-treated at 300˚C.
Figure 5.26: Kinetics plots for the 19-5-3 plate (a) widths and (b) thicknesses in the sample heat-treated at 350°C.
Figure 5.27: Kinetics plots for the 19-5-3 plate (a) widths and (b) thicknesses in the sample heat-treated at 400°C.
Figure 5.28: Kinetics plots for the 19-5-3 plate (a) widths and (b) thicknesses in the sample heat-treated at 450°C.
Figure 5.29: Kinetics plots for the 19-5-3 plate (a) widths and (b) thicknesses in the sample heat-treated at 475°C.
Figure 5.30: Kinetics plots for the 19-5-3 plate (a) widths and (b) thicknesses in the sample heat-treated at 500°C.
Figure 5.31: Plot of log $k$ against $1/T$ for the $k$ values obtained from the kinetic plots for coarsening of the 19-5-3 plates (Figures 5.25-30 for the plate widths and thicknesses).
temperature data are 201 and 145 kJ/mol, respectively. We note that somewhat better linear fits were obtained for the $\bar{a}_t^n - \bar{a}_i^n$ versus $t$ kinetic plots for the 475°C and 500°C heat-treatments if the 96 h data points were omitted; this gave lower values of $k$ for these temperatures and correspondingly lower values of $Q$ (147 and 120 kJ/mol) in the 450-500°C regime.

The values of $Q$ determined for the 300-400°C regime are up to an order of magnitude lower than those expected for Al self diffusion or lattice diffusion of Ni, Co, and Y in Al [102]. This suggests that short-circuit diffusion along dislocations and grain boundaries in the FCC Al phase is the rate-limiting mechanism for coarsening at these temperatures. Our TEM data indicate that the Al grain size is similar to the inter-particle separation of the 19-5-3 phase and that the dislocation density is extremely low in both phases. Thus, the very sluggish coarsening of the 19-5-3 phase in this regime can be explained on the basis of the large fluxes of Ni, Co and Y required and the low densities of short-circuit diffusion paths. The higher values of $Q$ determined for the 450-500°C regime suggest that there may be a transition to lattice diffusion being the rate-limiting mechanism at these temperatures. We note that the more rapid coarsening at these higher temperatures involves the formation of a secondary population of much larger 19-5-3 plates giving more bimodal particle size distributions. This transition in the particle size distribution resembles that for the development of abnormal grain growth in which certain grains develop at the expense of others due to differences in boundary energy, grain orientation or second-phase particle distribution. The origins of the abnormal 19-5-3 plate coarsening observed here are unclear. The large plates have the same chemistry, crystal structure and overall morphology as the smaller plates. Moreover, each 19-5-3
plate is surrounded by several Al grains and so there can be no simple crystallographic orientation relationship to drive the abnormal growth of particular plates. Since the alloy studied here is powder-processed, it is tempting to speculate that the abnormal coarsening may occur due to local inhomogeneities such as pores that could act as vacancy sources or impurities that could lead to incipient melting, but we have no evidence to support such hypotheses.

In this study it was necessary to use sequences of many BF TEM images such as Figures 5.21(a) – (g) to obtain accurate measurements of the Al grain size. These data were only acquired for the extrudate and the samples heat-treated for 96 h, and so we were not able to perform an analysis of the grain growth kinetics. The TEM images suggest that the Al grains are heavily pinned by the 19-5-3 phase and that the grain size will be dictated by the dispersion of the 19-5-3 phase. To demonstrate this we consider a very simple model for the inter-particle separation. Our previous studies have shown that the ratio of width to thickness for these plates is approximately 3.5:1, and the measurements obtained here suggest that this ratio does not change significantly in the normal coarsening regime. Moreover, the volume fraction of the 19-5-3 phase is essentially constant at 22%. On this basis, the measured values of plate width and thickness were used to determine the mean volume for the 19-5-3 particles and this was then converted to an equivalent radius, \( r \), for a spherical particle of the same volume. The mean inter-particle separation, \( \lambda \), was then calculated using the following expression for a random distribution of spherically shaped particles [103]:

\[
\lambda = \frac{4}{3} r \left( \frac{1}{F_v} - 1 \right)
\]
where \( F_v \) is volume fraction of the particles. The values of \( \lambda \) calculated from the particle dimensions in the samples heat-treated for 96 h are plotted against the measured Al grain sizes for these samples in Figure 5.32. There is a clear linear correlation between these values for the samples heat-treated at up to 450°C, i.e. in the normal coarsening regime. Although there are many simplifying assumptions used in this analysis, we note that several other expressions for \( \lambda \) also gave a good linear fit to \( d \), albeit with somewhat different slopes from that shown in Figure 5.32. The linear variation of \( \lambda \) with \( d \) breaks down at higher temperatures when abnormal coarsening occurs and the parameter \( \lambda \) is no longer physically meaningful since this assumes a single characteristic particle size.

Thus, we envisage several distinct stages in the development of the Al grain structure. Firstly, there is the formation of a distribution of FCC Al grains between the 19-5-3 plates during the consolidation/devitrification process. If at this stage the FCC grain size is less than the inter-particle separation then, as discussed previously for coarsening in such two-phase microstructures [104], one would expect rapid grain growth until the FCC Al phase domains are essentially single grains. Such a process could be responsible for the initial rapid softening of the alloy in the earliest stages of heat treatment. Thereafter, the Al grain size is dictated by the distribution of the 19-5-3 plates and thus further grain growth requires coarsening of the intermetallic plates. At lower temperatures (up to 400°C) rather sluggish normal coarsening of the plates occurs and so Al grain growth is limited. At higher temperatures, however, there is abnormal coarsening of the intermetallic plates and more extensive, if rather inhomogeneous, Al grain growth occurs.
Figure 5.32: Plot of the calculated inter-particle separation ($\lambda$) against measured Al grain size ($d$) obtained from the as-extruded material and from samples heat-treated at 300-500 °C for 96 h.
5.3 Conclusions

A study on the microstructure and hardness of a powder-processed Al - 3.71 Ni - 0.44 Co - 0.17 Zr - 2.95 Y (all in at.%) alloy consolidated by warm extrusion has shown:

1. The as-extruded material consists mainly of two phases: 22% by volume of Al$_{19}$(Ni,Co)$_3$Y$_3$ plates with the orthorhombic Al$_{19}$Ni$_5$Gd$_3$-type crystal structure, and a matrix of FCC Al grains. Each 19-5-3 plate is surrounded by several Al grains, so there is no well-defined orientation relationship between the phases, but the plates are aligned with their major axis parallel to the extrusion axis.

2. The hardness of the alloy decreases gradually from 163 VHN in the as-extruded material to 157 and 149 VHN in the samples heat-treated for 96 h at 300 and 350°C, respectively. The samples heat-treated at 400-500°C exhibit an initial rapid decrease in hardness after 2 h (146-122 VHN), but then the hardness gradually decreases to final values between 135 and 95 VHN.

3. The only changes in phase that occur upon heat-treatment are the appearance of up to 3 vol.% Al$_3$(Y,Zr) precipitates in samples heat-treated at 350°C and above. The majority of these are Al$_3$Y with the rhombohedral Ba$_3$Pb structure, but there is also a small amount of Al$_3$Zr with the D$_{0_{23}}$ structure.

4. For heat treatments at temperatures up to 450°C the 19-5-3 phase undergoes slow normal coarsening. For heat treatments at 475 and 500°C, the 19-5-3 phase undergoes abnormal coarsening with a second population of large plates developing rapidly.
5. The growth kinetics for the 19-5-3 plates gives a coarsening exponent of 3, as expected for Ostwald-type ripening. The activation energy for particle growth changes with temperature suggesting a transition from short circuit diffusion at 300-400°C to lattice diffusion at 450-500°C.

6. The Al grains appear to be pinned heavily by the 19-5-3 plates such that the Al grain size is dictated by the distribution of the intermetallic phase.

The excellent microstructural stability and limited softening of this alloy indicates that such materials could be utilized for structural applications at significantly higher temperatures than conventional Al alloys.
Chapter 6: Al-Mn-Ce Alloy

6.1 Results

6.1.1 Starting Microstructure

6.1.2 Effect of Heat-Treatment on Hardness

6.1.3 Development of Microstructure at 350°C

6.1.4 Effect of Temperature for 48h Heat-Treatments

6.2 Discussion

6.3 Conclusions
Chapter 6: Al-Mn-Ce Alloy

The following chapter contains the results, discussion and conclusions sections pertaining to the work performed on the Al-5Mn-2Ce (at.%) alloy.

6.1 Results

6.1.1 Starting Microstructure

The phases present in the gas-atomized powder and in the as-extruded material were first determined by XRD. Typical scans from these materials are presented in Figure 6.1, where the counts are plotted on a logarithmic scale to better show the low intensity peaks. In the data from the gas-atomized powder (Figure 6.1a), there is a relatively high background suggesting the presence of some residual amorphous phase. Peaks corresponding to the FCC Al and orthorhombic Al$_{11}$Ce$_3$ phases were identified, but the vast majority of the peaks did not correspond to any known phase(s) in the Al-Mn-Ce system. A search of known phases in other Al-TM-RE systems resulted in a match with Al$_{20}$Cr$_2$Ce; this phase exhibits the cubic Al$_{18}$Cr$_2$Mg$_3$ crystal structure with a 184-atom basis and a lattice parameter of 1.448 nm. All of the remaining peaks in Figure 6.1a could be accounted for as arising from a phase with this structure. From our subsequent electron microscopy analysis (see below) this phase was assigned the chemical formula Al$_{20}$Mn$_2$Ce, and Rietveld analysis of the XRD data gave mean phase volume fractions of 60.7% Al, 39.2% Al$_{20}$Mn$_2$Ce and 0.1% Al$_{11}$Ce$_3$ in the powder. We note that these are the relative proportions of the crystalline phases in the powder; the amorphous phase is not included since we were not able to determine the volume fraction of this phase. The data from the as-extruded material in Figure 6.1b revealed a more complex phase mixture.
Figure 6.1: XRD data obtained from samples of the (a) gas-atomized powder and the (b) as-extruded material. The counts are presented on a logarithmic scale to better reveal weak peaks from the minor phases. The symbols indicate peaks arising from the phases: FCC Al (circles), cubic Al$_{20}$Mn$_2$Ce (triangles), orthorhombic Al$_{11}$Ce$_3$ (squares), orthorhombic Al$_6$Mn (stars) and cubic Al$_{12}$Mn (hexagons).
consisting of the phases Al, Al$_{20}$Mn$_2$Ce, Al$_6$Mn, Al$_{12}$Mn and Al$_{11}$Ce$_3$. The lower and more uniform background in this case indicated that the samples had undergone complete devitrification with no residual amorphous material. After phase identification, Rietveld analysis of the diffraction pattern gave mean phase volume fractions of 41.6% Al, 36.3% Al$_{20}$Mn$_2$Ce, 19.3% Al$_6$Mn, 1.5% Al$_{12}$Mn and 1.3% Al$_{11}$Ce$_3$ in the extrudate. The crystallographic parameters for each of these phases are given in Table 6.1.

The distribution and morphology of the phases in the as-extruded material was further investigated by electron microscopy techniques. Figure 6.2a is a representative BSE SEM image, which exhibits strong contrast (i.e. distinctly different grey levels) between the phases due to the large differences in atomic number density. Complementary bright field (BF) TEM images, such as Figure 6.2b, revealed more clearly the morphology and grain size of each phase. Representative BF TEM images, zone axis selected area diffraction patterns (SADPs) and indexed schematics of the first-order maxima in the SADPs are shown for the intermetallic phases Al$_{20}$Mn$_2$Ce, Al$_{12}$Mn, Al$_6$Mn and Al$_{11}$Ce$_3$ in Figures 6.2c-f, respectively. EDXS data were also obtained from such particles (not shown) and standard-less quantification was performed using the thin film approximation. In each case, the values obtained were consistent with these phases adopting the stoichiometries implied by the chemical formulae. Grains of the Al$_{20}$Mn$_2$Ce phase (Figure 6.2c) are usually found in clusters and tend to be heavily twinned; they adopt an equi-axed morphology with diameters ranging from 170 – 690 nm. The Al$_{12}$Mn phase (Figure 6.2d) also adopts an equi-axed morphology with sizes ranging from 110 – 290 nm. The Al$_6$Mn phase exhibits a more elongated morphology with lengths and widths ranging from 98 – 300 and 50 – 210 nm, respectively. The fine particles found
Table 6.1: Crystallographic parameters for the five phases identified in the as-extruded material.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space Group</th>
<th>Prototype</th>
<th>Crystal Class</th>
<th>Lattice Parameters (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Fm$\bar{3}$m</td>
<td>Cu</td>
<td>Cubic</td>
<td>$a = 0.405$</td>
<td>[105]</td>
</tr>
<tr>
<td>Al$_6$Mn</td>
<td>Cmcm</td>
<td>Al$_6$Mn</td>
<td>Orthorhombic</td>
<td>$a = 0.755$ $b = 0.650$ $c = 0.887$</td>
<td>[106,107]</td>
</tr>
<tr>
<td>Al$_{12}$Mn</td>
<td>Im$\bar{3}$</td>
<td>Al$_{12}$W</td>
<td>Cubic</td>
<td>$a = 0.747$</td>
<td>[108]</td>
</tr>
<tr>
<td>Al$_{11}$Ce$_3$</td>
<td>Imm$ar{m}$</td>
<td>Al$_{11}$La$_3$</td>
<td>Orthorhombic</td>
<td>$a = 0.440$ $b = 1.303$ $c = 1.009$</td>
<td>[109]</td>
</tr>
<tr>
<td>Al$_{20}$Mn$_2$Ce</td>
<td>Fd$\bar{3}$m</td>
<td>Al$_{18}$Cr$_2$Mg$_3$</td>
<td>Cubic</td>
<td>$a = 1.448$</td>
<td>[110]</td>
</tr>
</tbody>
</table>
Figure 6.2: Electron microscopy data from samples of the as-extruded material. (a) and (b) BSE SEM and BF TEM images showing the overall morphology and distribution of the phases. (c)-(f) BF TEM images, zone axis SADPs and indexed schematics of the SADPs obtained from regions containing particles of: (c) Al$_{20}$Mn$_2$Ce with $\mathbf{B} = [112]$; (d) Al$_{12}$Mn with $\mathbf{B} = [111]$; (e) Al$_6$Mn with $\mathbf{B} = [\overline{1}10]$; and (f) Al$_{11}$Ce$_3$ with $\mathbf{B} = [31\overline{1}]$; these are the dark particles in the center of the BF images in each case. The regions numbered 1-4 in (a) correspond to examples of the intermetallic phases Al$_{20}$Mn$_2$Ce, Al$_{12}$Mn, Al$_6$Mn and Al$_{11}$Ce$_3$, respectively.
throughout the microstructure are the Al\textsubscript{11}Ce\textsubscript{3} phase (Figure 6.2f); these are present both as equi-axed particles with diameters of 30 – 110 nm and as elongated particles with lengths and widths of 70 – 165 and 40 – 75 nm, respectively. The uniform bright background in the BF TEM images is the Al matrix, which has a grain size of 400 – 600 nm. The combination of TEM imaging, diffraction and EDXS analysis not only confirmed the presence of the phases identified by XRD, but also allowed an unambiguous correlation to be established between the BSE SEM image contrast and the corresponding phases. Therefore, in Figure 6.2a, the dark background corresponds to the Al matrix, the bright patches (e.g. at 1) are the Al\textsubscript{20}Mn\textsubscript{2}Ce phase, the two intermediate shades of grey are the Al\textsubscript{12}Mn and Al\textsubscript{6}Mn phases (e.g. at 2 and 3, respectively) and the fine, very bright particles are the Al\textsubscript{11}Ce\textsubscript{3} phase (e.g. at 4).

6.1.2 Effect of Heat-Treatment on Hardness

The effects of heat-treatment on the mechanical response of the alloy were evaluated using Vickers hardness testing. Figure 6.3 is a plot of the hardness values (Vickers hardness number – VHN) obtained from samples heat-treated at 300, 350, 400, 450 and 500 °C for times of 2, 8, 24, 48 and 96 h. Each data point represents the mean of 3 measurements; for clarity, error bars are not shown on the figure, but in each case the variability in the data was less than ±5 VHN. The hardness of the as-extruded material is 204 VHN, which is denoted by the data point at 0 hours. There was no significant variation in hardness with heat-treatment at 300°C. For heat-treatments at 350°C there was a slight decrease in hardness to 197 VHN after 2 h, but then the hardness value increased steadily with heat-treatment time to a value of 297 VHN after 96 h. The
Figure 6.3: Mean values of Vickers micro-hardness data from the as-extruded material (denoted by the star at 0 h) and the materials heat-treated at 300 – 500°C for 2, 8, 24, 48 and 96 h. The lines through these data points for each heat-treatment temperature are intended as a guide for the eye.
material heat-treated at 400°C exhibited a rapid increase in hardness to values of 213 and 269 VHN after 2 and 8 h, respectively. With further exposure at 400°C, the hardness increased more gradually reaching a value of 304 VHN after 96 h; this is the highest hardness value obtained for any of the heat-treatments performed in this study. The material heat-treated at 450°C exhibited an even more rapid increase in hardness with values of 247 and 283 VHN after 2 and 8 h, respectively, but the hardness did not then vary significantly with continued exposure. A dramatic change in the mechanical response was measured for the material heat-treated at 500°C. The hardness decreased continuously with time reaching a value of 128 VHN after 48 h with no significant change thereafter. This is the lowest hardness value obtained for any of the heat-treatments performed in this study.

To investigate the microstructural origins of these interesting trends in the mechanical behavior of the material, two sets of specimens were selected for detailed microstructural characterization experiments. The first set contained the five samples heat-treated at 350°C for 2, 8, 24, 48 and 96 h. The second set consisted of the five samples heat-treated for 48 h at 300, 350, 400, 450 and 500 °C.

6.1.3 Development of Microstructure at 350°C

The effects of exposure time on the alloy microstructure for heat treatments performed at 350°C was first investigated using XRD. The data acquired from the samples were quantified by Rietveld analysis where crystallographic texture effects were accounted for by using March–Dollase model. The only phases found in these heat-treated samples are the ones identified in Table 6.1, and the mean volume fractions of the
phases determined from the XRD data are plotted against heat-treatment time in Figure 6.4. The data for the as-extruded material are included as the points at 0 h on this plot. The volume fraction of the FCC Al phase decreased gradually with exposure time from 41.6% in the extrudate to 12.7% after 48 h, but there was no further change in the amount of this phase after 96 h. The changes in the volume fraction of the Al$_{20}$Mn$_2$Ce phase were more dramatic; this fell from an initial value of 36.3% to 2% after 8 h, and the phase was not observed after longer exposure times. The volume fraction of the Al$_6$Mn phase initially increased from 19.3% (as-extruded) to 28% after 2 h and then fell gradually to 1.2% after 96 h. There was a corresponding increase in the volume fractions of the Al$_{11}$Ce$_3$ and Al$_{12}$Mn phases, which rose from 1.3% and 1.5%, respectively in the as-extruded material to 13% and 72%, respectively after 96 h. We note that the Al$_{11}$Ce$_3$ phase reached this final volume fraction much sooner (8 h) than the Al$_{12}$Mn phase (48 h).

The distributions and morphologies of these phases were investigated using SEM and TEM techniques as before. For brevity, we present here only BSE SEM images of the microstructures, and representative examples of such images from the samples heat-treated at 350˚C for 2, 8, 24, 48 and 96 hours are shown in Figures 6.5a-e, respectively. The contrast from the various phases in these images is the same as that described for the corresponding image from the as-extruded material (Figure 6.2a). In Figures 6.5a and 6.5b there are regions containing a fine mixture of Al$_{12}$Mn and Al$_{11}$Ce$_3$ phases adjacent to the Al$_{20}$Mn$_2$Ce phase, and it appears that the phase mixture is growing to consume the Al$_{20}$Mn$_2$Ce phase with this transformation being complete after 24 h (Figure 6.5c). At this point, the microstructure is a four-phase mixture of Al$_{12}$Mn (dark grey), Al$_{11}$Ce$_3$ (bright particles), Al (black patches) and some residual Al$_6$Mn (light grey). The main
Figure 6.4: Values of the phase volume fractions determined by Rietveld analysis of the XRD pattern from the as-extruded material (denoted as 0 h) and materials heat-treated at 350°C for 2, 8, 24, 48 and 96 h.
Figure 6.5: Representative BSE SEM images obtained from the materials heat-treated at 350°C for: (a) 2 h, (b) 8 h, (c) 24 h, (d) 48 h and (e) 96 h. The contrast in these images is similar to that in Figure 2a such that the phases are (going from black to white): Al, Al_{12}Mn, Al_{6}Mn, Al_{20}Mn_{2}Ce and Al_{11}Ce_{3}.
changes in the microstructure beyond this point are a coarsening of the FCC Al, Al₁₂Mn and Al₁₁Ce₃ phases, and a decrease in the amount of the Al₆Mn phase. After 96 h these phases still exhibited their original morphologies with grain sizes for the FCC Al, Al₁₂Mn and Al₆Mn ranging from 800 – 1200 nm, 900 – 1200 nm, and 150 – 200 nm, respectively. For the Al₁₁Ce₃ phase, the equi-axed particles ranged from 70 – 530 nm and the elongated particles had lengths and widths ranging from 250 – 350 nm and 140 – 250 nm, respectively.

6.1.4 Effect of Temperature for 48h Heat-Treatments

The effects of temperature on the alloy microstructure for heat-treatments performed at 300, 350, 400, 450 and 500°C for 48 hours were first investigated by XRD. For the samples heat-treated at 300, 350, 400, and 450°C, the only phases present were those identified in Table 6.1. The volume fractions of these phases are shown in Figure 6.6; here again these were obtained by Rietveld analysis with crystallographic texture effects accounted for using the March–Dollase model. For comparison, the corresponding values for the as-extruded material are shown as horizontal bars on the ordinate axis. The volume fraction of the FCC Al phase decreased gradually from 41.6% in the extrudate to 12.7% in the sample heat-treated at 350°C, but there was no further significant change in this value with increased heat-treatment temperature. There was a more substantial change in the volume fraction of the Al₂₀Mn₂Ce phase; its value fell from 36.3% in the extrudate to 13.4% in the sample heat-treated at 300°C, and this phase was not observed for higher heat-treatment temperatures. For the Al₆Mn phase the volume fraction increased from 19.3% in the extrudate to 29.1% in the sample heat-treated at 300°C, but
Figure 6.6: Values of the phase volume fraction determined by Rietveld analysis of the XRD pattern from the as-extruded material (denoted by the horizontal bars on the ordinate axis), and the materials heat-treated for 48 h at 300, 350, 400 and 450°C.
then decreased to 2.4% in the sample heat-treated at 350°C and was not observed in samples heat-treated at 400 and 450°C. There was an increase in the volume fraction of the Al$_{11}$Ce$_3$ phase from 1.3% in the as-extruded sample to 11.4% in the sample heat-treated at 300°C, but the samples heat-treated at 350-450°C all exhibited similar volume fractions of this phase (11.4-14.1%). Similarly, the volume fraction of the Al$_{12}$Mn phase rose from 1.3% in the extrudate to 14.6% and 72.1, respectively in the samples heat-treated at 300 and 350°C. There was no further significant change in the volume fraction of the Al$_{12}$Mn phase for samples heat-treated at 400 and 450°C. For the sample heat-treated at 500°C, however, additional strong peaks were observed, and these peaks were not consistent with any known equilibrium or metastable phase in the Al-Mn-Ce system, or indeed any of the other Al-TM-RE systems that we considered. The XRD data from the material heat-treated at 500°C for 48 h are shown in Figure 6.7. The symbols used to denote the FCC Al, Al$_{11}$Ce$_3$, Al$_6$Mn and Al$_{12}$Mn phases are the same as those in Figure 6.1, and here again the counts are plotted on a logarithmic scale to better show the low intensity peaks. The unidentified peaks are marked by asterisks, as are those showing anomalously high intensity suggesting additional contributions from another phase. Further information on this unknown phase is given below.

The distributions and morphologies of these phases were investigated using SEM and TEM techniques as before. Representative BSE SEM images of the microstructures in samples heat-treated at 300, 350, 400, 450 and 500°C for 48 h are shown at the same magnification in Figures 6.8a-e, respectively and Figure 6.8f is a lower magnification BSE image of the material heat-treated at 500°C. The microstructure in the sample heat-treated at 300°C for 48 h (Figure 6.8a) is similar to that after 8 h at 350°C (Figure 6.5b),
Figure 6.7: XRD data obtained from material heat-treated at 500°C for 48 h. The counts are presented on a logarithmic scale to better reveal weak peaks from the minor phases. The symbols indicate peaks arising from the phases: FCC Al (circles), orthorhombic Al$_{11}$Ce$_3$ (squares), orthorhombic Al$_6$Mn (stars), cubic Al$_{12}$Mn (hexagons) and the unidentified Al$_3$(Mn,Ce) compound (asterisks).
Figure 6.8: Representative BSE SEM images obtained from the materials heat-treated for 48 h at: (a) 300°C, (b) 350°C, (c) 400°C, (d) 450°C, (e) and (f) 500°C.
in that there are regions containing a fine mixture of $\text{Al}_{12}\text{Mn}$ and $\text{Al}_{11}\text{Ce}_3$ phases adjacent to, and apparently growing to consume, the $\text{Al}_{20}\text{Mn}_2\text{Ce}$ phase. This transformation appears to be complete in the material heat-treated for 48 h at 350°C as shown in Figure 6.8b. At this point, the microstructure is a four-phase mixture of $\text{Al}_{12}\text{Mn}$ (dark grey), $\text{Al}_{11}\text{Ce}_3$ (bright particles), Al (black patches) and some residual $\text{Al}_{6}\text{Mn}$ (light grey). The only changes in the microstructure for samples heat-treated at 400 and 450°C (Figures 6.8c and 6.8d, respectively) are a coarsening of the $\text{Al}_{12}\text{Mn}$ and $\text{Al}_{11}\text{Ce}_3$ phases and a decrease in the amount of the $\text{Al}_{6}\text{Mn}$ phase. The morphologies and sizes of the phases in the materials heat-treated up to 450°C were broadly consistent with those observed in the material heat-treated at 350°C for 96 h, where the FCC Al and $\text{Al}_{12}\text{Mn}$ phases had grain sizes ranging from 1 – 2 µm. For the $\text{Al}_{11}\text{Ce}_3$ phase, the majority of the particles were equi-axed with diameters ranging from 100 – 400 nm with occasional elongated particles exhibiting lengths and widths as large as 700 and 300 nm, respectively. Grains of the $\text{Al}_{6}\text{Mn}$ phase were no larger than 200 nm. Images such as Figure 6.8e obtained at the same magnification from the sample heat-treated at 500°C for 48 h appeared to show a more severely coarsened version of the same microstructure, but lower magnification BSE SEM images (e.g. Figure 6.8f) revealed the appearance of a new microstructural constituent: large blocky regions of a light grey phase whose contrast lies between that for $\text{Al}_{6}\text{Mn}$ and $\text{Al}_{11}\text{Ce}_3$. The composition of this new phase measured by EDXS was 75 at. % Al and 25 at. % (Mn + Ce). The Al content was consistent from one region to another, but the proportions of Mn and Ce in this ternary phase varied somewhat, with some indications of a preference for Mn:Ce ratios of 3:2 and 2:3. Thus, the material consists mainly of a matrix of FCC Al plus the $\text{Al}_3(\text{Mn,Ce})$ ternary phase with $\text{Al}_6\text{Mn}$ and
Al\textsubscript{12}Mn as minority phases and occasional small particles of Al\textsubscript{11}Ce\textsubscript{3}. Here the grain sizes for the FCC Al, Al\textsubscript{12}Mn and Al\textsubscript{6}Mn phases ranged from 1000 – 1900 nm, 600 – 1700 nm, and 500 – 1500 nm, respectively. For the Al\textsubscript{11}Ce\textsubscript{3} phase, only equi-axed particles were observed with diameters ranging from 60 – 180 nm. The Al\textsubscript{3}(Mn,Ce) phase exhibited lengths and widths ranging from 1600 – 6900 nm and 240 – 1700 nm, respectively. Occasional equi-axed Al\textsubscript{3}(Mn,Ce) grains were observed with diameters ranging from 1500 – 2700 nm.

Complementary low-magnification BF TEM images, such as Figure 6.9a, revealed more clearly the morphology and grain size of each phase. In particular, such images showed that each of the blocky regions of the ternary phase observed in BSE SEM images such as Figure 6.8f was composed of several adjacent grains. Most of these grains were elongated parallel to the major axis of the blocky ternary phase regions and they frequently exhibited banded contrast similar to that which one might expect for high densities of stacking faults, twins and/or incommensurate intergrowths. Three examples of higher-magnification BF TEM images are presented in Figures 6.9b-d. In each case the inset SADPs were obtained from the ternary phase grain in the center of the corresponding field of view. We note that none of these zone axis SADPs, or indeed any of the other patterns obtained from this phase, exhibited mirror symmetry. This indicates that the phase probably exhibits a low-symmetry structure (monoclinic or triclinic), but we were not able to identify the structure unambiguously. An exhaustive search was performed for known Al-rich phases with stoichiometries close to Al\textsubscript{3}X and which also exhibited low-symmetry crystal structures. None of these phases gave a good match to both the TEM and XRD data from these samples. A reasonable fit to the zone axis
Figure 6.9: TEM data of the material heat-treated at 500°C for 48 h: (a) low-magnification BF image showing the overall morphology and distribution of the phases; (b-d) BF images with inset zone axis SADPs obtained from the ternary phase particles in the center of each image.
SADPs in Figures 6.9b-d was obtained for two candidate structures: monoclinic Al$_3$Fe ($a$ = 1.5489 nm, $b$ = 0.80831, $c$ = 1.2476 and $\beta$ = 107.72° [111]) and triclinic Al$_{11}$Mn$_4$ ($a$ = 0.5095 nm, $b$ = 0.8879 nm, $c$ = 0.5051 nm, $\alpha$ = 85.35°, $\beta$ = 100.47° and $\gamma$ = 105.08° [112]). However, in both cases these structures could not account for all of the strong unknown peaks in the XRD data from the samples heat-treated at 500°C.

Since the structure of the Al$_3$(Mn,Ce) ternary phase is not known, it was not possible to establish the phase volume fractions by Rietveld analysis from the XRD pattern. However, by analyzing several BSE SEM images such as Figure 6.8(f), and relating these to the phase morphologies observed by TEM, we estimate the volume fractions as approximately: 60% FCC Al, 22% Al$_3$(Mn,Ce), 9% Al$_{12}$Mn, 8% Al$_6$Mn and 1% Al$_{11}$Ce$_3$.

### 6.2 Discussion

The original objective of this investigation was to study the formation, stability and effect on mechanical behavior of quasi-crystalline phases in this relatively dilute alloy. However, in contrast to previous reports [22-26] of icosahedral quasi-crystals being formed in alloys with this composition, no such phases were observed in any of our samples. One possible explanation for this is suggested by the work of Inoue et al. on melt-spun Al-Mn-Ce ribbons, in which it was shown that Al-5Mn-2Ce (at.%) lies close to the boundary between the formation of a single-phase FCC Al solid solution and the formation of quasi-crystals in an FCC Al matrix [18]. This implies that quasi-crystal formation is only marginally favored in alloys with this composition, and therefore the
cooling rates for the metal droplets in the gas atomization process used here may not be high enough to lead to the formation of these phases.

Our XRD data (Figure 6.1) show that the gas-atomized powder is instead a mixture of amorphous and crystalline phases. The latter phases are: FCC Al (60.7%), a small amount (0.1%) of the equilibrium Al$_{11}$Ce$_3$ phase and a much larger amount (39.2%) of a ternary phase Al$_{20}$Mn$_2$Ce; this latter phase exhibits the cubic Al$_{18}$Cr$_2$Mg$_3$ structure and a lattice parameter of $a_0 = 1.448$ nm. Although several different Al$_{20}$Cr$_2$X compounds (where X = Ca, Ce, Er, Gd, Ho, La, Nd, Pr or Y) with this structure were identified by Krypyakevich and Zarechnyuk [113], as far as we are aware this is the first time that such a compound has been reported in an Al-Mn-X system. During consolidation by warm extrusion there was complete devitrification of the powder, presumably due to a combination of the pre-heat and any adiabatic heating that occurred on passing through the extrusion die. The resulting microstructure consisted mainly of FCC Al (41.6%), Al$_{20}$Mn$_2$Ce (36.3%) and Al$_6$Mn (19.3%), with a small amount (< 2% each) of Al$_{12}$Mn and Al$_{11}$Ce$_3$.

Upon heat treatment the volume fraction of the Al$_{20}$Mn$_2$Ce phase decreased rapidly and for higher temperatures and/or longer times this phase was eliminated from the microstructure, i.e. this is a metastable phase at these temperatures. For short heat-treatment times there was an increase in the volume fraction of the Al$_6$Mn phase, but for higher temperatures and/or longer times this phase was also eliminated. For longer heat-treatments (48 and 96 h) at 350-450°C, the microstructures consisted of over 72-73% by volume Al$_{12}$Mn plus roughly equal proportions (13-14% each) of Al$_{11}$Ce$_3$ and FCC Al. The only differences in the microstructures were the sizes of the grains/particles, which
coarsened with increased time/temperature, suggesting that this is close to an equilibrium phase mixture at these temperatures. Upon heat-treatment at 500˚C, however, a rather different phase mixture developed; the dominant phases were FCC Al, Al₁₂Mn, Al₆Mn and Al₃(Mn,Ce), with the latter exhibiting an as-yet unidentified low-symmetry structure. The Al₁₁Ce₃ phase was also present as a minority constituent.

We note the Al₁₂Mn + Al₁₁Ce₃ + Al phase mixture formed upon heat-treatment at 350-450˚C gave the highest hardness values measured from this alloy, and so the Al₁₂Mn must be extremely hard despite being the most Al-rich of the intermetallic phases observed. The formation of Al₁₂Mn was not anticipated, particularly as a majority phase, since Al₆Mn appears as the most Al-rich equilibrium phase in most published binary Al-Mn and ternary Al-Mn-Ce phase diagrams (e.g. [114] and [115], respectively). Indeed Al₁₂Mn was frequently reported to be a metastable compound in such systems [116-118], and this was only observed as a minority constituent in the presence of a more abundant Al₆Mn phase [119-121]. Subsequent thermodynamic evaluations of the binary Al-Mn system identified Al₁₂Mn as an equilibrium phase [122, 123] that forms via a peritectoid reaction between FCC Al and Al₆Mn at around 510˚C. Such peritectoid reactions are notoriously sluggish, and, to our knowledge, the only direct experimental evidence for this process is the study conducted by Schaefer et al [124] on melt-spun ribbons of an Al-7.4 at.% Mn alloy. The as-spun samples exhibited a single-phase FCC structure, but this decomposed rapidly to give a mixture of FCC Al + Al₆Mn upon heat-treatment, but then the peritectoid transformation proceeded much more slowly. Thus, for heat treatments at 400˚C the decomposition to FCC Al + Al₆Mn was complete in 1 h, but the onset of the peritectoid was not detected until after 24h and this transformation took 1000 h to reach
completion. In the present work, the stable $\text{Al}_{12}\text{Mn} + \text{Al}_{11}\text{Ce}_3 + \text{Al}$ phase mixture was established after just 24h at 400˚C. There are two possible explanations for this phenomenon. Firstly, the stability of the binary Al-Mn phases could be influenced strongly by the presence of Ce as suggested recently by Mula et al. [125] in their studies on mechanically alloyed Al-Mn-Ce alloys. Secondly, the easy formation of $\text{Al}_{12}\text{Mn}$ might be due to an energetically favorable transformation pathway. In the present alloy the $\text{Al}_{12}\text{Mn}$ phase forms by the decomposition of a metastable $\text{Al}_{20}\text{Mn}_2\text{Ce}$ phase, and indeed the presence of finely divided mixtures of $\text{Al}_{12}\text{Mn}$ and $\text{Al}_{11}\text{Ce}_3$ could suggest that this occurs by a co-operative process akin to eutectoid decomposition. If we assume that all of the compounds adopt their stoichiometric compositions then the balanced equation for this process would be:

$$3\ \text{Al}_{20}\text{Mn}_2\text{Ce} + 23\ \text{Al} \rightarrow 6\ \text{Al}_{12}\text{Mn} + \text{Al}_{11}\text{Ce}_3$$

Thus, a large Al flux would be required to sustain this process. We note that if $\text{Al}_{20}\text{Mn}_2\text{Ce}$ were to decompose to form $\text{Al}_6\text{Mn}$ instead, then a three-phase mixture would be expected:

$$3\ \text{Al}_{20}\text{Mn}_2\text{Ce} \rightarrow 6\ \text{Al}_{12}\text{Mn} + \text{Al}_{11}\text{Ce}_3 + 13\ \text{Al}$$

Since the latter process does not occur, it seems more likely that the formation of $\text{Al}_{12}\text{Mn}$ is favored thermodynamically by the presence of Ce.

This raises the intriguing possibility that the Al-Mn-Ce system could form the basis for a novel heat-treatable Al alloy. The $\text{Al}_{12}\text{Mn}$ phase has a much higher Al:TM ratio than most of the strengthening phases utilized in commercial Al alloys, and thus one would expect a higher volume fraction of the intermetallic phase for a given alloying content. Moreover, based upon our observations, it appears that $\text{Al}_{12}\text{Mn}$ would be an
effective strengthening phase because it has a high hardness. Thus an alloy with a fine
distribution of this phase could exhibit a high strength at a low total solute content and
(depending upon the amount of Ce required) a low cost. One would also expect the
\( \text{Al}_{12}\text{Mn} \) phase to be a stable structure up to temperatures of at least 450°C, although it is
not clear how resistant the phase would be to coarsening at such temperatures.

6.3 Conclusions

A study of the microstructural development and hardness of a powder processed
\( \text{Al-5Mn-2Ce} \) (all in at.%) alloy consolidated by warm extrusion has shown:

1. No quasicrystalline phases are formed in contrast to previous reports on rapidly
solidified alloys with similar compositions.

2. The gas atomized powder consisted of an amorphous phase, FCC Al, a little
\( \text{Al}_{11}\text{Ce}_{3} \), and a previously unreported phase, \( \text{Al}_{20}\text{Mn}_{2}\text{Ce} \), which exhibits the cubic
\( \text{Al}_{18}\text{Cr}_{2}\text{Mg}_{3} \) crystal structure with a lattice parameter of 1.448 nm.

3. Upon consolidation the extrudate devitrifies fully to give a mixture of FCC Al,
\( \text{Al}_{20}\text{Mn}_{2}\text{Ce} \) and \( \text{Al}_{6}\text{Mn} \), with a small amount of \( \text{Al}_{12}\text{Mn} \) and \( \text{Al}_{11}\text{Ce}_{3} \). The
\( \text{Al}_{20}\text{Mn}_{2}\text{Ce} \) and \( \text{Al}_{6}\text{Mn} \) phases decompose upon subsequent heat-treatment at 300-500°C indicating that they are metastable under these conditions.

4. For heat treatment temperatures of up to 450°C the decomposition products are
\( \text{Al}_{12}\text{Mn} \) and \( \text{Al}_{11}\text{Ce}_{3} \), and a stable phase mixture is formed consisting of 72-73%
\( \text{Al}_{12}\text{Mn} \) plus 13-14% each of \( \text{Al}_{11}\text{Ce}_{3} \) and FCC Al. This phase mixture is
significantly harder than the extrudate (280-310 VHN c.f. 204 VHN).
5. For heat treatments at 500°C an Al$_3$(Mn, Ce) phase with an unknown low symmetry structure is formed instead, and the microstructure consists of: 60% FCC Al, 22% Al$_3$(Mn, Ce), 9% Al$_{12}$Mn, 8% Al$_6$Mn and 1% Al$_{11}$Ce$_3$. This phase mixture is much softer at around 128 VHN. Since Al$_{12}$Mn usually forms extremely slowly via a peritectoid reaction between Al and Al$_6$Mn in binary Al-Mn alloys, it appears that Ce stabilizes the Al$_{12}$Mn phase in this ternary alloy. This phase exhibits high hardness, good thermal stability and is the most Al-rich phase observed in the system. Thus, more dilute Al-Mn-Ce compositions could form the basis for new high-strength, low-density Al-based alloys with enhanced elevated temperature properties.
Chapter 7: Summary and Future Work

7.1 Al-Ni-Y based Alloy

7.2 Al-Mn-Ce based Alloy
Chapter 7: Summary and Future Work

The work presented in this dissertation has shown trends in the microstructural development and the associated mechanical response for two Al-Transition Metal-Rare Earth alloys, both of which were produced via identical powder metallurgical techniques. These two alloys exhibit excellent phase stability and vastly improved elevated temperature properties as compared to commercially available Al-based alloys. The findings open up potential opportunities in the development of new, high strength low density Al alloys. Possible future direction for research on these systems include the following:

7.1 *Al-Ni-Y based Alloy*

Previous studies on this alloy system have established the microstructures and their development with heat-treatment and thermal-mechanical processing such as forging. Other important properties that should be investigated are the machinability and weldability of these materials. These parameters are very important to understand if one were to manufacture components from these alloys. In addition, further investigations on the fatigue and creep behavior on these alloys should be carried out. These properties become increasingly important if these materials are to be used at elevated temperature and in regions under cyclic loading.

7.2 *Al-Mn-Ce alloy*

Contrary to what has been reported in the literature, the work presented in this dissertation revealed that no quasicrystalline phases were formed in the powder or the extrudate. Instead, the formation of the metastable Al$_{20}$Mn$_2$Ce phase was reported, which
decomposed subsequently with heat-treatment to form of a high volume fraction of \( Al_{12}Mn \). If one were to consider these findings, then there are two possible directions that future studies could take. The first involves further pursuing the original intent for this study, which was the development of an material consisting of quasicrystalline particles in an Al matrix on the industrial scale. This would involve increasing the solute concentration to help promote the formation of the quasicrystalline metastable phase in the gas-atomized powder. Upon successful formation of this phase in the powder, subsequent consolidation experiments would need to be carried out to determine the appropriate extrusion conditions that would yield a high quality billet and still retain the quasicrystalline phase. If successful, then investigations could be carried out on the microstructural development with heat-treatment and the corresponding changes to mechanical behavior.

The second possible direction would be to exploit the conclusion that Ce appears to stabilize the hard \( Al_{12}Mn \) phase. This study showed that just a small amount of Mn and Ce led to the formation of >70% by volume of the \( Al_{12}Mn \) phase. A series of alloys with lower solute concentrations could be produced, which would effectively reduce the volume fraction of the \( Al_{12}Mn \) phase. Then one could attempt to development of a thermal-mechanical process that would promote the direct formation of \( Al_{12}Mn \) phase. If a fine dispersion of the hard and thermally stable \( Al_{12}Mn \) phase could be formed within an Al matrix, then this alloy could constitute a new series of high-strength Al-rich alloys with enhanced elevated temperature properties. Subsequent investigations could be carried out to study the coarsening behavior of this phase and the associated changes to the mechanical behavior such as tensile, fatigue and creep properties.
References


[63] Latuch J, Matyja H, Fadeeva VI (1994) Crystallization of amorphous Al$_{85}$Y$_{10}$Ni$_5$ and Al$_{85}$Y$_{5}$Ni$_{10}$ alloys, Mater Sci Eng A 179:506-510


[71] Inoue A, Kimura HM, Masumoto T, Tsai AP, Bizen Y, Al-Ge-(Cr or Mn) and Al-Si-(Cr or Mn) Quasicrystals with High Metalloid Concentration Prepared by Rapid Quenching, J Mater Sci Let 6: 771-774


