EFFECT OF HOMOGENIZATION ON THE MICROSTRUCTURAL DEVELOPMENT IN A D.C. CAST AA3104 ALUMINUM ALLOY USED FOR CANBODY STOCK

by

CHETAK GANDHI
B. Tech., Indian Institute of Technology, Kharagpur, India, 1994

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Department of Metals and Materials Engineering)

We accept the thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1999

© Chetak Gandhi, 1999
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Metals & Materials Engg
The University of British Columbia
Vancouver, Canada

Date 27 April 1999
Abstract

As customer demands become more stringent for canbody stock, it becomes essential to understand the complex interaction between the processing conditions and resulting product properties. This research focused on investigating the influence of homogenization process parameters (heat-up rate, soak temperature and time) on the microstructural evolution of an AA3104 aluminum alloy used for canbody stock. Experiments were conducted on samples taken from an industrial D.C. cast ingot and homogenized in a programmable temperature controlled laboratory furnace under various thermal profiles (i.e. homogenization temperatures 550°C, 580°C and 610°C at various heating rates and homogenization soak times of up to ten hours). The samples were then characterized in terms of their microstructure (retained manganese in solid solution, percentage α-phase, and size distribution and density of dispersoids).

The homogenization process parameters were found to affect the evolving microstructure profoundly with:

- An increase in heat-up rate favoring a reduction in the number of evolving dispersoids.
- An increase in soak temperature increasing the Mn in solid solution, and decreasing the number of dispersoids that form.
- An increase in soak time up to 3 hrs increasing the volume percent of α-Al$_{12}$(Fe,Mn)$_3$Si.

Based on this work, a homogenization profile for optimum microstructure and texture development would include a fast heat-up rate to a high soak temperature (610°C) with moderate soak times (up to 3 hrs).
# Table of Contents

Abstract ........................................................................................................................................... ii

Table of Contents ....................................................................................................................... iii

List of Figures .............................................................................................................................. vi

List of Tables .............................................................................................................................. ix

Acknowledgements .................................................................................................................. x

1 Introduction .............................................................................................................................. 1

2 Literature Review .................................................................................................................... 5

2.1 Industrial Can Making Operation ....................................................................................... 5

2.2 Solidification - As-cast Microstructure .............................................................................. 6

2.3 Microstructural Changes During Homogenization .............................................................. 10

2.3.1 Equilibration of Alloying Elements and Removal of Microsegregation ................... 11

2.3.2 Precipitation of Dispersoids ......................................................................................... 14

2.3.3 Modification of As-Cast Constituent Phases ................................................................. 15

2.3.4 Mn in Solid Solution ..................................................................................................... 17

2.4 Effect of Composition on the As-Cast and Homogenized Microstructure .................... 19

2.4.1 Silicon .......................................................................................................................... 19

2.4.2 Iron ............................................................................................................................ 20

2.4.3 Copper ........................................................................................................................ 20

2.4.4 Magnesium ................................................................................................................ 21

2.4.5 Manganese ................................................................................................................ 22
List of Figures

Figure 1.1 - Aluminum beverage can demand [1]. 1

Figure 1.2 - Typical processing sequence for the production of final gauge sheet [3]. 3

Figure 2.1 - Photomicrographs showing the size and shape of the constituents in as-cast ingot at: (a) edge and (b) center locations [12]. 7

Figure 2.2 - Diffusion coefficients for various elements in aluminum at different temperatures [18]. 12

Figure 2.3 - Effect of 0.06% Fe and 0.02% Cu on the loss of supersaturation in Al-1 Mn Alloys at 550°C [30]. 21

Figure 2.4 - Mn precipitation vs. time and temperature for an as-cast 3104 alloy [34]. 25

Figure 2.5 - Mn content in α-phase constituents as a function of homogenization temperature [26]. 27

Figure 2.6 - Examples of secondary precipitates in TEM thin foil specimens of AA3004 alloy at (a) 600°C and (b) 560°C [27]. 28

Figure 2.7 - TEM photomicrographs showing the α-dispersoids in ingot homogenized at 577°C for (a) 14 hrs and (b) 26 hrs, followed by water quench [12]. 30

Figure 4.1 - Laboratory furnace set-up: a) overview and b) cross-sectional view. 38

Figure 4.2 - Experimental homogenization profiles with varying heat-up rates (dots indicating where samples were taken for microstructure characterization). 40

Figure 4.3 - Experimental homogenization profiles with varying soak temperatures (550°C, 580°C and 610°C). 40

Figure 4.4 - Experimental thermal profiles used for samples homogenized at different soak temperatures. 41

Figure 4.6 - Resistivity of aluminum alloy 3004 as a function of the percentage of Mn in solid solution [43]. 43

Figure 4.7 - As-cast microstructure (1000X) showing the various second phase particles. 45

Figure 4.8 - EDX/SEM results confirming the etching difference between α-Al12(Fe,Mn)3Si and Al6(Fe,Mn) particle. 46
Figure 4.9 - Variation of the cumulative average per field with the measured quantity per field for volume fraction second phase.

Figure 5.1 - Effect of heat-up rate on %Mn in solid solution.

Figure 5.2 - Effect of heat-up rate on % $\alpha$-Al$_{12}$(Fe,Mn)$_3$Si after a 3 hour hold at 580°C.

Figure 5.3 - Microstructures of samples for 580°C soak temperature after 3 hour hold for: a) 279°C/hr and b) 47°C/hr.

Figure 5.4 - Microstructures of samples at 450°C during heat-up for: a) 279°C/hr and b) 47°C/hr.

Figure 5.5 - Mn in solid solution at different soak temperatures at a) 47°C/hr and b) 279°C/hr.

Figure 5.6 - Effect of soak temperature on % $\alpha$-Al$_{12}$(Fe,Mn)$_3$Si after a soak period of three hours.

Figure 5.7 - Effect of soak time on % $\alpha$-Al$_{12}$(Fe,Mn)$_3$Si at various soak temperatures at a heat-up rate of 47°C/hr.

Figure 5.8 - Microstructures (1000X) of samples after three hour hold with a heat-up rate of 47°C/hr for soak temperatures of: a) 550°C, b) 580°C and c) 610°C.

Figure 5.9 - Mn in solid solution for homogenization profiles of 550°C, 580°C and 610°C for three hour hold followed by cool down to 500°C.

Figure 5.10 - Microstructures (1000X) of samples after a cool down to 500°C for soak temperatures of: a) 550°C, b) 580°C and c) 610°C.

Figure A1 - Temperature variations between furnace (580°C) and sample of original furnace at a) two sample positions in the furnace, and b) on a raised platform near the furnace thermocouple.

Figure A2 - Temperature variations between furnace (580°C) and sample temperature in the retrofitted furnace.

Figure B1 - Microstructures of samples at 580°C soak temperature after 3 hr hold for a) 37°C/hr, b) 47°C/hr, c) 70°C/hr, d) 112°C/hr, and e) 279°C/hr.

Figure C1 - EPMA line scans (Mg and Mn) for the as-cast microstructure.

Figure C2 - EPMA line scans (Mg and Mn) for 47°C/hr profile at a) 400°C, b) 500°C, 580°C (0 hrs), and d) 580°C (3hrs).
Figure C3 - EPMA line scans (Mg and Mn) for 279°C/hr profile at a) 400°C, b) 500°C, 580°C (0 hrs), and d) 580°C (3hrs).
List of Tables

Table 1.1 - Mechanical properties of aluminum sheet in H19 condition. 2
Table 2.1 - Nominal weight percent composition of selected 3xxx alloys. 5
Table 2.2 - Size variation of cells and stringers with various casting methods [13]. 8
Table 2.3 - Relative solid solubility and rate of diffusion of major alloying elements in 3xxx series alloys [10]. 12
Table 2.4 - Effects of homogenization treatment and Si content on α-phase constituents (i.e. α-Al₁₂(Fe,Mn)₃Si) [4]. 16
Table 2.5 - Change in α-Al₁₂(Fe,Mn)₃Si dispersoid mean size during preheat heat-up and soak [16]. 29
Table 4.1 - Composition of AA3104 alloy used. 37
Table 4.2 - Range of homogenization process parameters used in the study. 39
Table 4.3 – Composition of AA3104 and effect of elements on resistivity [18]. 42
Table 4.4 - Grinding and polishing procedure followed. 44
Table 4.5 - As-cast characterization between 5 - 25 cm from surface. 49
Table 5.1 - Minimum Mn in solid solution and corresponding temperature for different heat-up rates. 52
Table 5.2 - Mn and Mg segregation results for 47°C/hr and 279°C/hr profile at various temperatures during heat-up. 58
Acknowledgements

I would like to thank, firstly, my advisor, Dr. Mary A. Wells, for her constant support and encouragement throughout this work.

I would also like to thank NSERC, Canada and Alcan International Ltd. for the material and financial help, and Dr. D. J. Lloyd (KRDC, Alcan Int. Ltd.) for many useful discussions and suggestions.

Special thanks to Mr. Ross Mcleod and Mr. Carl Ng for preparing all my samples, to Mr. Rudy Cardeno for the image analysis work, to Ms. Mary Mager for her instructions and advice with the SEM, to Mr. Serge Millare for the help with the furnace and other electrical issues, and to Peter Musil for help with the furnace repair and fittings.

I would like to convey many thanks to Mr. Gary Lockhart for his help with experimental set-up and valuable advice and Rob Stevenson for his help in the project.

Finally, this work would not have been completed without the encouragement and support of my family and friends.
1 Introduction

Over the last decade there has been considerable growth in the use of aluminum alloys for rigid packaging of food products, with the most significant increase being in the beverage container market. The world market for beverage containers has seen a steady rise over the last ten years [1] (Figure 1.1). The continuing strong demand for aluminum alloys in this very competitive market is forcing aluminum sheet producers to critically examine their production processes in terms of both cost and final material properties.

Figure 1.1 - Aluminum beverage can demand [1].
Aluminum beverage cans are deep drawn from the final cold rolled sheets of AA3004 or AA3104 aluminum alloys [2, 3]. These alloys are essentially Al-Mn-Mg alloys also containing Cu, Si and Fe. The current demand is for AA3104 final canbody sheet that is ≤ 0.3 mm gauge and with strength corresponding to the H19 condition (Table 1.1)

Table 1.1 - Mechanical properties of aluminum sheet in H19 condition.

<table>
<thead>
<tr>
<th>Tensile strength (UTS)</th>
<th>295 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Strength</td>
<td>285 MPa</td>
</tr>
<tr>
<td>Elongation</td>
<td>2%</td>
</tr>
</tbody>
</table>

Besides strength, elongation and gauge, another important requirement for the final sheet is its crystallographic texture. Undesirable textures in the sheet leads to “earing” which may cause trouble during can making as well as yield losses as they must be trimmed off. The phenomenon of “earing” refers to undulations on the rim of cups formed during cup drawing or wall ironing, the high points named as “ears”. During processing, earing is controlled by balancing two types of textures; i.e., by developing a strong cube texture (0-90° earing) upon recrystallization after hot rolling followed by the superposition of a rolling texture (45°-45° earing) during subsequent heavy cold rolling to final gauge [4, 5, 6]. The resulting product will not show zero earing, but rather small mixed ears of similar size.
Typically processing of Direct Chill (D.C.) cast aluminum ingots (generally 300 - 760 mm thick) to final gauge sheet (~0.3 mm thick) for the beverage can market involves a number of processing steps (Figure 1.2).

The process steps include:

i) homogenization (temperatures above ~550°C and soaked for a controlled period).

ii) breakdown rolling (the temperature falls from ~500°C to ~300°C and the ingot is reduced to a slab of ~25 mm thickness).

iii) tandem rolling (multiple stand continuous mill with 3-4 stands produce coiled metal ~2.5 mm thick that recrystallizes without furnace annealing).
iv) cold rolling (~87% reduction in thickness to final sheet with ≤ 0.3 mm thick).

v) final heat treatment.

One area in sheet production that plays a crucial role in the final sheet gauge properties of canbody stock is homogenization. Homogenization, also known as pre-heating, is typically used to:

(i) remove microsegregation of alloying elements in the ingot and

(ii) raise the ingot temperature for hot rolling.

The most economical way to run this process would be to have a cycle as short as possible and at as low a temperature as possible. Balanced with this is the need to produce an optimum microstructure capable of producing the desired properties in the final gauge sheet.

In addition, the microstructure of the homogenized ingot can influence the strength, formability and the texture of the final gauge sheet for the canbody stock. Some of the important microstructural features in the as-homogenized ingot include relatively large constituent particles, fine dispersoids that are precipitated during processing and the solute levels in solid solution [7]. Each of these can affect the recrystallization process and in particular, the strength of the cube texture after hot deformation, which is of paramount importance in controlling anisotropy in the final product [5, 8]. In an effort to understand and quantify the microstructural changes that occur during homogenization, this study examined the effect of the homogenization process on key microstructural features.
2 Literature Review

2.1 Industrial Can Making Operation

The manufacture of beverage cans is one of the most demanding sheet applications for aluminum [9]. The primary alloys used for canbody stock are AA3004 and AA3104, which are non-heat-treatable aluminum alloys. The nominal specification for these alloys is given in Table 2.1 but typically beverage manufacturers operate on much tighter specifications than those given. AA3004 and AA3104 are essentially the same alloys with the exception of the tighter Mn range in AA3004.

Table 2.1 - Nominal weight percent composition of selected 3xxx alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA3004</td>
<td>0.8-1.3</td>
<td>1.0-1.5</td>
<td>0.7 max.</td>
<td>0.3 max.</td>
<td>0.25 max.</td>
</tr>
<tr>
<td>AA3104</td>
<td>0.8-1.3</td>
<td>0.8-1.4</td>
<td>0.8 max.</td>
<td>0.4 max.</td>
<td>0.05-0.25</td>
</tr>
</tbody>
</table>

Conventional body stock for beverage cans is produced from 600 to 750 mm diameter ingots by semi-continuous direct-chill (D.C.) casting or electromagnetic casting (EMC) processes. Other methods for casting canbody stock that have been tried experimentally but are currently not widely used are: (a) continuous casting of 13 to 25
mm thick slabs by introducing liquid metal between parallel mold surfaces (e.g., the Hazelett water-cooled steel belt casters, Alusuisse Caster II and Lauener block casters which employ large metal chill blocks) (b) continuous casting of 6 to 12 mm thick strips produced by introducing liquid metal between water cooled rolls, followed by cold rolling to final gauge without any preheating or hot rolling (e.g., Pechiney Jumbo 3C caster and the Hunter process).

2.2 Solidification - As-cast Microstructure

The as-cast microstructure defines the starting structure for the study of microstructure evolution during homogenization. The cast structure of AA3xxx consists of a cellular dendritic aluminum matrix with stringers containing intermetallic phases along the cell boundaries, remnants of the last highly segregated melt to freeze (Figure 2.1). The main features defining the cast structure are: (a) the cell size and intermetallic particle size, (b) the degree of solute supersaturation, and (c) the morphology of the intermetallics. Due to the thickness of the ingot, the freezing rate varies from the edge to the center (Figure 2.1) [10, 11, 12]. The freezing rate can also vary greatly based on the casting practices. As the freezing rate during casting increases, the dendrite cell size decreases while the stringers become thinner and envelop the cell boundaries more continuously (Table 2.2). The cell size plays an important role in the equilibration process of the alloying elements and the spatial arrangement of the precipitating dispersoids during homogenization. Typically, the finer the cell size the smaller the distance which the elements must travel within the cell and therefore homogenization.
occurs more quickly and the precipitate stringers tend to be finer yet engulf the cells more continuously [10, 11, 12].

Figure 2.1 - Photomicrographs showing the size and shape of the constituents in as-cast ingot at: (a) edge and (b) center locations [12].
Table 2.2 - Size variation of cells and stringers with various casting methods [13].

<table>
<thead>
<tr>
<th>Shape</th>
<th>Process</th>
<th>Thickness (mm)</th>
<th>Freezing Rate- edge (°C/s)</th>
<th>Cell Size (μm)</th>
<th>Stringer thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingot</td>
<td>D.C.*</td>
<td>660</td>
<td>1</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>Billet</td>
<td>D.C.*</td>
<td>200</td>
<td>10</td>
<td>45</td>
<td>0.7</td>
</tr>
<tr>
<td>Slab</td>
<td>Belt/Block</td>
<td>19</td>
<td>20</td>
<td>30</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Stationary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strip</td>
<td>Mold</td>
<td>13</td>
<td>100</td>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>Strip</td>
<td>Twin Mold</td>
<td>6</td>
<td>700</td>
<td>6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*NOTE: The freezing rate at the center of a D.C. cast ingot is ~0.25°C/sec whereas at the edge is ~1°C/sec [13].

The intermetallic phases that form in AA3104 consist of two major types: orthorhombic Al₆(Fe,Mn) and cubic α-Al₁₂(Fe,Mn)₃Si. The relative amounts of these phases are determined by the alloy composition as well as the solidification rate [11, 12, 14, 15]. In AA3104 under commercial D.C.-cast ingot cooling rates of about 1°C/s (Table 2), about 85% of the primary constituent particles in the as-cast structure correspond to the Al₆(Fe,Mn) phase and the remainder to α-Al₁₂(Fe,Mn)₃Si [14]. At these cooling rates, about 25-30% of the Mn precipitates out of solid solution in the form of intermetallic particles during solidification while the rest of the Mn (~70-75%) remains in solid solution, thereby producing an as-cast structure which is in a supersaturated metastable...
solid solution condition [14]. Moreover, the as-cast structure exhibits microsegregation of Mg, Si, and to a lesser extent Mn, across the dendritic cellular cast structure [16].

The formation of phases and the temperatures at which they nucleate during the solidification process of AA3004 have been summarized by Backerud et al [17]. Initially as the molten aluminum begins to cool and its temperature reaches ~648-652°C the liquid will begin to solidify and form an aluminum dendritic matrix according to:

1. Liquid (L) $\rightarrow$ Al, dendritic network @ 648-652°C

The first constituent particles Al$_6$(Fe,Mn) start to nucleate at the periphery of the growing dendrites at ~643°C according to the eutectic phase transformation 2:

2. Liquid (L) $\rightarrow$ Al + Al$_6$(Fe,Mn) @ 643°C

At lower temperatures (~638°C), a peritectic reaction occurs between the (Mn,Fe)Al$_6$ particles and the remaining liquid which has been enriched in Si according to 3a:

3a. Liquid (L) + Al$_6$(Fe,Mn) $\rightarrow$ $\alpha$-Al$_{12}$(Fe,Mn)$_3$Si @ 638°C

As the liquid continues to be enriched in solute the $\alpha$-Al$_{12}$(Fe,Mn)$_3$Si phase can form directly from it according to 3b:

3b. Liquid (L) $\rightarrow$ Al$_{12}$(Fe,Mn)$_3$Si @ 638°C

Finally, at slightly lower temperatures, eutectic $\beta$-Mg$_2$Si particles precipitate from the melt given the high Si and Mg in the alloy according to 4:

4. Liquid (L) $\rightarrow$ Al + Al$_{12}$(Fe,Mn)$_3$Si + Mg$_2$Si @ 630°C

Homogenization, which occurs after casting of the ingot, modifies the as-cast microstructure significantly and has a direct influence on both the hot-rolled and cold-
rolled sheet properties. As a result it is important to understand the microstructural changes which occur during homogenization, the effect of homogenization parameters on the microstructure evolution and how this behaviour can be represented mathematically.

2.3 Microstructural Changes During Homogenization

During homogenization, the D.C. cast ingot is heated and soaked at a temperature in the range of about 10-100°C below the solidus for the alloy and 20-100°C above the desired initial hot working temperature. For AA3xxx alloys, the solidus ranges from 630-645°C, homogenization temperatures are typically 530-620°C and the initial hot rolling temperatures are 480-520°C [10].

The basic purpose of the homogenization process is to reduce microsegregation that exists in the as-cast ingot as well as preheat the ingot to the desired hot rolling temperature. Concurrent with the constitutional equilibration and reduction in microsegregation of some elements in solid solution during homogenization, several other microstructural changes occur in the matrix, such as:

i) precipitation of supersaturated elements as dispersoids,

ii) dissolution of unstable phases or precipitates,

iii) transformation of $\text{Al}_6(\text{Fe,Mn})$ to $\alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$, and

iv) coarsening of the stable intermetallic particles.
2.3.1 Equilibration of Alloying Elements and Removal of Microsegregation

Microsegregation in the as-cast ingot and equilibration of alloying elements during homogenization depend upon a number of factors: their solid solubility in the aluminum matrix, their rate of diffusion in the aluminum matrix for the element and the cell size of the cast microstructure. In AA3xxx aluminum alloys both Mn and Fe have relatively low solubility in the aluminum matrix and hence they tend to be the elements which will be in a supersaturated condition in the as-cast aluminum matrix (Table 2.3). During homogenization, the supersaturation of Mn and Fe within the dendritic cells is largely relieved by the precipitation of fine (Fe,Mn)-rich dispersoids consisting primarily of Al$_{12}$(Mn,Fe)$_3$Si phase [16], or Al$_6$(Mn,Fe) if the Si content is less than about 0.07 wt% [4].

In the as-cast aluminum structure both Mg and Si will exhibit a significant amount of microsegregation or coring across the dendritic cellular as-cast microstructure. The segregation pattern existing in the as-cast microstructure will be unstable as it is heated up to and held at the homogenization temperature and equilibration of these elements will begin to occur during heat-up to the homogenization soak temperature. In fact, by the time the ingot has reached 500°C, the Mg and Si levels have typically homogenized completely across the cell [16].
Table 2.3 - Relative solid solubility and rate of diffusion of major alloying elements in 3xxx series alloys [10].

<table>
<thead>
<tr>
<th>Solubility and Diffusion Rate</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate solubility, Low diffusion rate</td>
<td>Mn,</td>
</tr>
<tr>
<td>Appreciable solubility, High diffusion rate</td>
<td>Cu, Mg, Si</td>
</tr>
<tr>
<td>Extremely low solubility, Very low diffusion rate</td>
<td>Fe</td>
</tr>
</tbody>
</table>

Figure 2.2 - Diffusion coefficients for various elements in aluminum at different temperatures [18].
The mechanism behind the homogenization process is diffusion and Mn and Fe have much lower diffusion coefficients (Figure 2.2). Since most Fe stays out of solid solution, the rate determining element is Mn. Diffusion of Mn is influenced by both temperature and time and can be described mathematically by Fick's law:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

This equation states analytically how the concentration (C) will change with time (t) according to a temperature dependent constant D which is called the diffusion coefficient. D depends on the temperature according to the Arrhenius equation:

\[
D = D_0 \exp^{-Q/RT}
\]

Where:

- \(D_0\) = constant
- \(Q\) = activation energy (kJ/mole)
- \(R\) = gas constant (8.314 J/mole°K)
- \(T\) = temperature (°K)

It is this exponential dependence on temperature that causes diffusional removal of concentration gradients to take place more rapidly at higher temperatures. Since this
process is governed entirely by diffusion, three main factors will determine the time needed for this to occur:

i) temperature,

ii) the actual values of $D_0$ and $Q$ in the Arrhenius equation which will differ for different elements, and

iii) the cell size of the cast microstructure since this will determine the distance over which diffusion must take place.

### 2.3.2 Precipitation of Dispersoids

Dispersoids are secondary precipitates that form during homogenization as a result of supersaturation of particular elements in the matrix. In AA3xxx alloys, these dispersoids are mostly $\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$, or sometimes $\text{Al}_6(\text{Fe,Mn})$ if the Si is lower than 0.08% in the ingot [4, 10, 16]. The formation of these precipitates during the homogenization process is a complex procedure involving the nucleation of the new phase into the aluminum matrix followed by growth until all of the excess solute has been consumed. In AA3xxx aluminum alloys, as the ingot is heated above 300°C, needles of and more sparsely distributed square platelets of $\beta$-$\text{Mg}_2\text{Si}$ begin to precipitate in the Al matrix [16]. At a slightly higher temperature of around 400°C, precipitates of $\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$ begin to nucleate on the pre-existing $\beta$-$\text{Mg}_2\text{Si}$ needles which subsequently dissolve as the temperature is increased. As the temperature is further increased, $\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$ dispersoids continue to precipitate while the existing precipitates begin to grow through coarsening mechanisms. Both the volume fraction and average size of dispersoids increases until ~480°C when the Mn precipitation rates peak.
Above that temperature, re-dissolution of dispersoids take place due to increased solid solubility of Mn in Al at higher temperatures \([4, 16, 20]\). The re-dissolution of dispersoids causes their number to decrease, however, those dispersoids that remain do undergo growth \([16]\). This shows that while the dispersoids nucleation period stops at \(~480^\circ\text{C}\), the growth period continues at higher temperatures.

Subsequent cooling from the peak preheating temperature to the hot rolling temperature causes renewed precipitation and growth of \(\alpha-\text{Al}_2\text{(Fe,Mn)}_3\text{Si}\) dispersoids. The final average size of dispersoids depends on the homogenization profile and can vary from 50nm to about 0.5\(\mu\text{m}\) in diameter \([4, 16, 19]\).

### 2.3.3 Modification of As-Cast Constituent Phases

The iron-rich intermetallic particles which form during solidification \((\text{Al}_6\text{(Fe,Mn)})\) are not removed during homogenization since the alloy is never heated into a single phase field and the diffusion coefficient of Fe in aluminum is so low. However, some changes, which are both time and temperature dependent, in the as-cast constituent particles do begin to occur during the homogenization process:

i) \(\text{Al}_6\text{(Fe,Mn)}\) starts to transform to \(\alpha-\text{Al}(\text{Fe,Mn})\text{Si}\), and

ii) Spherodization of the particles.

Between 480\(^\circ\text{C}\) and 593\(^\circ\text{C}\), the normally dominant \(\text{Al}_6\text{(Fe,Mn)}\) constituent phase gradually transforms to \(\text{Al}_2\text{(Fe,Mn)}_3\text{Si}\) phase. This transformation occurs due to localized enrichment of the matrix with Si, originally present in the form of \(\text{Mg}_2\text{Si}\) in the as-cast microstructure but which dissolves during the early stages of the homogenization
process. The transformation is initiated by nucleation of $\alpha$-$\text{Al}_2(\text{Fe,Mn})_3\text{Si}$ at the interface between $\text{Al}_6(\text{Fe,Mn})$ and the solute enriched matrix [21]. The $\alpha$-$\text{Al}_2(\text{Fe,Mn})_3\text{Si}$ phase then grows into and consumes the $\text{Al}_6(\text{Fe,Mn})$ particles. Depending on the composition of the alloy, this transformation can either go quickly to completion or be stopped before completion because of a lack of Si. In order for this reaction to proceed, Mn and Si must diffuse through the matrix, and the rate of the reaction is usually controlled by Mn diffusion. If Si is tied up as $\text{Mg}_2\text{Si}$, due to high Mg or low Si, the transformation is slowed down due a lack of Si. In general, this transformation is promoted by a higher Si content and a higher homogenization temperature (Table 2.4) [4, 22, 23].

Table 2.4 - Effects of homogenization treatment and Si content on $\alpha$-phase constituents (i.e. $\alpha$-$\text{Al}_2(\text{Fe,Mn})_3\text{Si}$) [4].

<table>
<thead>
<tr>
<th>Simulated Homogenization Treatment</th>
<th>Percent of $\alpha$-$\text{Al}_2(\text{Fe,Mn})_3\text{Si}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.21% Si Ingot</td>
</tr>
<tr>
<td>As-cast</td>
<td>10</td>
</tr>
<tr>
<td>Heated to 427°C</td>
<td>10</td>
</tr>
<tr>
<td>Heated to 482°C</td>
<td>25</td>
</tr>
<tr>
<td>Heated to 538°C</td>
<td>50</td>
</tr>
<tr>
<td>Heated to 566°C</td>
<td>70</td>
</tr>
<tr>
<td>Heated to 593°C</td>
<td>85</td>
</tr>
<tr>
<td>Heated to 616°C</td>
<td>85</td>
</tr>
<tr>
<td>Heated to 632°C</td>
<td>50</td>
</tr>
<tr>
<td>Heated to 638°C</td>
<td>0</td>
</tr>
</tbody>
</table>
The exact significance of the transformation of $\text{Al}_6(\text{Fe,Mn})$ to $\alpha$-$\text{Al(Fe,Mn)}\text{Si}$ is not completely understood although an increased level of $\alpha$-$\text{Al(Fe,Mn)}\text{Si}$ has been reported to improve the drawing and ironing behaviour in canmaking; the $\alpha$-$\text{Al(Fe,Mn)}\text{Si}$ particles are harder than the $\text{Al}_6(\text{Fe,Mn})$ particles and help in cleaning the dies thereby prevent galling [4].

The constituent particles can also change their morphology during homogenization. Initially, the particles have a plate-like elongated and irregular shape with a high surface area. During homogenization, spherodization of particles can start to take place as the elongated particles break up into smaller fragments having a more globular appearance [16, 24, 25].

### 2.3.4 Mn in Solid Solution

The level of Mn in solid solution after the homogenization process for AA3xxx alloys can influence the properties of the final gauge sheet. During the homogenization process, the amount of Mn in solid solution will initially drop as Mn precipitation rates peak at temperatures between 475°C and 500°C depending on the alloy composition [4, 16, 20]. As the temperature is further increased, the amount of Mn in solid solution increases as the solubility of Mn in the matrix increases. At the end of homogenization, however, there is considerably less Mn in solid solution than in the as-cast microstructure.

Mn depletion in the solid solution takes place in three ways:

i) Precipitation of Mn-rich dispersoids.
ii) Transformation of $\text{Al}_6(\text{Fe},\text{Mn})$ to $\alpha-\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$: Total $(\text{Fe}+\text{Mn})$ in $\text{Al}_6(\text{Fe},\text{Mn})$ is about 25 wt.% compared with 32 wt.% of $(\text{Fe}+\text{Mn})$ in $\alpha-\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ phase [4, 26, 27]. With very little Fe available in the matrix, it is mostly achieved through Mn enrichment.

iii) Enrichment of Mn in both dispersoids and eutectic constituents [10, 26, 27].

During homogenization, Mn is known to diffuse into the particles thereby increasing the %Mn in both $\text{Al}_6(\text{Fe},\text{Mn})$ [10] and $\alpha-\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ [26, 27] particles. Hence, though the $(\text{Fe}+\text{Mn})/\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ ratio of the particles stays fairly constant, the Mn/(Fe+Mn) increases with an increase in homogenization temperature or decrease in cell size of the ingot.
2.4 Effect of Composition on the As-Cast and Homogenized Microstructure

The exact composition of the alloy will have a significant influence on both the structure that forms during solidification of the ingot as well as some of the microstructural changes which occur during the homogenization process.

2.4.1 Silicon

Commercial producers of beverage canbody stock presently have between 0.12% and 0.30% Si in their alloys. Varying silicon in the ingot affects the developing microstructure in the following ways.

i) **Effect on constituent particles**: an increase in percentage of Si in the alloy gives a higher percentage of $\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ in the as-cast structure and also promotes the transformation of $\text{Al}_6(\text{Fe,Mn})$ to $\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ during various stages of homogenization treatment [4, 28] (Table 2.4).

ii) **Effect on Mn solubility**: Si enhances the precipitation of Mn as well as other constituent elements such as Fe and Mg.

Increasing Si reduces the amount of Mn in solid solution in the as-cast as well as homogenized ingot [4, 28]. Si reduces Mn content in solid solution by causing a higher proportion of $\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ to form, thereby removing more Mn from solid solution (Table 2.4). While $\text{Al}_6(\text{Fe,Mn})$ contains about 25 wt% ($\text{Fe + Mn}$), $\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ contains about 32 wt% [26].
iii) **Effect on Dispersoids:** As mentioned earlier, the dispersoids formed are mostly \( \alpha \)-\( \text{Al}_2(\text{Fe,Mn})_3\text{Si} \), but if Si is below 0.08%, the dispersoids which form are of the type \( \text{Al}_6(\text{Fe,Mn}) \).

### 2.4.2 Iron

The effect of iron is very pronounced in an Al-Mn-Si alloy. Even a very small addition of Fe to the Al-Mn alloy greatly enhances the number of constituent particles which form facilitating the Mn precipitation and preventing the formation of the ternary metastable phases \( \text{Al}_x\text{Mn}_y\text{Fe}_z \) usually encountered in the Al-Mn-Fe alloys [29]. No ternary precipitation phase appears, but rather Fe atoms substitute for Mn atoms in \( \text{Al}_6\text{Mn} \). During homogenization, Mn enters \( \text{Al}_6(\text{Fe,Mn}) \) until the phase has achieved its maximum stability at \( \text{Al}_6(\text{Fe}_{0.5},\text{Mn}_{0.5}) \) [29]. Iron additions influence the number of constituent particles which form and this will have a direct impact of the recrystallization kinetics and texture which forms in hot rolled sheet as particle stimulated nucleation (PSN) becomes more dominant.

### 2.4.3 Copper

Copper has a very similar though milder effect than iron. Both copper and iron promote Mn precipitation in aluminum alloys. The effect of 0.06 Fe and 0.20 Cu on the loss of Mn supersaturation in Al-1 Mn alloys at 550°C is shown in Figure 2.3 [30].
2.4.4 Magnesium

Magnesium (Mg) contributes to the overall strength of the alloy through solid solution hardening and work hardening [31]. AA3004/AA3104 have often been considered as non-heat-treatable Al-Mn alloys to which Mg is added to improve its work hardening characteristics. Furthermore, a comparison of similar AA3xxx alloys indicates that the Mg containing AA3104 requires substantially less homogenization time than the equivalent AA3003 without Mg [32]. This has been explained by the role of Mg$_2$Si matrix precipitation acting as nucleation sites for $\alpha$-dispersoids during the early stages of ingot heating [4, 16, 32].
2.4.5 Manganese

Mn in canbody stock provides large hard particles effective in die-cleaning during drawing operations. It also imparts some strength to the final gauge sheet through solution hardening and excellent corrosion resistance [33].

Varying the Mn content of the ingot from 0.6wt% to 0.9wt% will give a higher Mn in solid solution throughout the homogenization process [26]. However, the resulting microstructure, in terms of volume fraction and size distribution of constituent particles and precipitation and dissolution of dispersoids, is not significantly different.
2.5 Effect of Homogenization Process Parameters on Microstructure

Although studies have been completed over the past decade [10, 24, 25, 34] in an effort to understand the effect of the homogenization profile on the microstructural evolution, the ability to predict an optimum homogenization profile for a given starting structure and alloy composition has not yet been developed. In fact, currently, industry uses a wide variety of homogenization profiles to process the same alloy even though the starting structure and chemistry may be very similar. Industrial homogenization profiles can vary significantly in terms of the soak temperature and time as well as the overall homogenization profile (i.e, a second stage soak at a lower temperature after the primary soak is complete). The final microstructure of the as-cast material after homogenization is chiefly dependent on the type of thermal profile (temperature and time) it has undergone. The parameters that can be varied in any thermal profile are:

- heat-up rate,
- soak temperature,
- soak time, and
- cool down rate.

Each of these process parameters can affect the microstructural evolution during the homogenization process.
2.5.1 Heat-up Rate

Currently, industrial heat-up rates during homogenization of ingot material typically range from around 45°C/hr (soaking pit furnace) to around 70°C/hr (walking beam furnace)[35]. To date, almost no research has been done on the effect of heat-up rate on the microstructure evolution or properties of homogenized canbody stock material. Sheppard [36] was the only researcher who studied the effect of heat-up rate on the microstructure evolution of a 7xxx series alloy. His findings showed that a slower heat-up rate to homogenization temperature had no influence on the constituent particles however that it did affect the dispersoid size and distribution, with the slower heating rate giving more dispersoids with a more homogeneous distribution. His results were explained using classical precipitate nucleation theory; a slower ramp provided a longer period within the temperature zone corresponding to maximum nucleation rates hence more dispersoids could precipitate. Later during the soak period at the homogenization temperature, precipitate growth and precipitate nucleation become competing processes whereby pre-existing nuclei grew at the expense of further nucleation.

2.5.2 Soak Temperature

Currently, the homogenization soak temperature for AA3xxx alloys used in the industry lies between 560°C and 610°C [35]. The ingots are heated to the soak temperature and held at this temperature for a period of time to achieve the desired microstructure. Soak temperature also known as the homogenization temperature, impacts most aspects of the microstructure such as:
i) percentage Mn in solid solution,
ii) constituent particles, and
iii) dispersoids.

Goodrich [34] investigated the effect of soak temperature on the final homogenized structure and percent Mn left in solid solution. He estimated the Mn in solid solution using resistivity measurements (Figure 2.4).

Figure 2.4 - Mn precipitation vs. time and temperature for an as-cast 3104 alloy [34].
As shown, after around 550°C, the difference between resistivity values (%Mn in solid solution) for 1 hr and 200 hrs is not very different indicating that Mn equilibration rates are sufficiently faster at those temperatures. It can also be inferred from the graph that equilibrium Mn in solid solution rises with an increase in temperature above 480°C. This temperature can be referred to as the peak Mn precipitation temperature since at this temperature there is least amount of Mn in solid solution. This is due to the higher solubility of Mn in Al at higher temperatures [4, 16, 34].

Constituent particles undergo a variety of changes as the homogenization temperature is raised over the peak Mn precipitation temperature such as:

(i) \( \text{Al}_6(\text{Fe,Mn}) \) to \( \alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si} \) transformation.

(ii) Particle coarsening and spherodizing.

(iii) Mn enrichment in particles.

The effect of temperature on \( \text{Al}_6(\text{Fe,Mn}) \) to \( \alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si} \) transformation can be estimated from Table 2.4. It is clear that an increase in temperature increases the \( \%\alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si} \) up to 593°C for both Si levels. At higher temperatures of 632°C and 638°C, where incipient melting takes place, transformation kinetics become greatly enhanced and a reduction in the \( \%\alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si} \) is seen in the lower Si alloy.

The constituent particles have shown a rounding of their edges (spherodization), coarsening and break up of the three-dimensional dendritic network when held at higher homogenization temperatures [22, 37, 27].

With an increase in homogenization temperatures, the Mn levels in particles is known to stabilize at different levels (Figure 2.5) [26]. Sun [26] suggested that it was
possible to determine the homogenization temperature from the composition of the eutectic constituents.

![Figure 2.5 - Mn content in α-phase constituents as a function of homogenization temperature [26].](image)

Quite a few researchers [10, 12, 16, 26, 27] have found that dispersoids that form during ingot heating become fewer and coarser as homogenization temperature increase.
There are fewer and coarser dispersoids present in a sample homogenized at 600°C than one homogenized at 560°C (Figure 2.6) [27].

Figure 2.6 - Examples of secondary precipitates in TEM thin foil specimens of AA3004 alloy at (a) 600°C and (b) 560°C [27].

Bolingbroke [16] has characterized the increase in size of the dispersoids with increase in temperature during heat-up (Table 2.5). It is clear that dispersoid coarsening is a direct function of temperature.
Table 2.5 - Change in $\alpha$-$\text{Al}_1\text{Fe}_2\text{Mn}_3\text{Si}$ dispersoid mean size during preheat heat-up and soak [16].

<table>
<thead>
<tr>
<th>Preheat treatment</th>
<th>Average $\alpha$-$\text{Al}_1\text{Fe}_2\text{Mn}_3\text{Si}$ precipitate size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>-</td>
</tr>
<tr>
<td>Heat-up to 400°C</td>
<td>35</td>
</tr>
<tr>
<td>Heat-up to 450°C</td>
<td>47</td>
</tr>
<tr>
<td>Heat-up to 500°C</td>
<td>66</td>
</tr>
<tr>
<td>Heat-up to 600°C</td>
<td>108</td>
</tr>
<tr>
<td>Heat-up to 600°C, cooled to 500°C at 30°C/hr</td>
<td>136</td>
</tr>
<tr>
<td>Heat-up to 600°C, soaked for 8 hrs and cooled to 500°C at 30°C/hr</td>
<td>150</td>
</tr>
</tbody>
</table>

2.5.3 Soak time

The soak time at the high temperature allows the reaction kinetics to proceed. Both Mg and Si have a high diffusion coefficient and will equilibrate even as the temperature reaches the homogenization temperature. Mn on the other hand, has a low diffusion coefficient and it is the rate determining step for the transformation of $\text{Al}_6(\text{Fe,Mn})$ to $\alpha$-$\text{Al}_1\text{Fe}_2\text{Mn}_3\text{Si}$ and dispersoid precipitation during the homogenization treatment. As the homogenization temperature increases, the time required for
homogenization decreases [12, 38]. This is partly because the Mn diffusion rates become faster and also partly because the equilibrium Mn in solid solution is higher at higher temperature. Besides Mn equilibration, time at homogenization temperature also allows for precipitate coarsening. For example, there is no change in Mn level for an ingot homogenized at 577°C for 14 hrs and for 26 hrs but TEM microstructures shows that α-dispersoids are almost twice the size after 26 hrs at 577°C [12](Figure. 2.7)

![Figure 2.7 - TEM photomicrographs showing the α-dispersoids in ingot homogenized at 577°C for (a) 14 hrs and (b) 26 hrs, followed by water quench [12].](image)

2.5.4 Second Stage Soak

Traditionally, industrial homogenization cycles consisted of heating the ingot to a prescribed temperature and holding it there for a certain length of time followed by air
cool to the hot rolling temperature. Recently, researchers have investigated the merit of altering the traditional homogenization cycle to include a second soak period at a lower temperature on the microstructural evolution in the ingot [26, 39]. Hence, a typical two stage homogenization profile consists of heat-up, hold at high temperature (560°C - 610°C) followed by controlled cooling to a lower temperature (450°C - 500°C) and a soak at this temperature prior to hot rolling.

One major difference in microstructure after a second stage soak is the lower Mn in solid solution compared to a traditional homogenization profile [39]. During the second stage cool, Mn precipitation occurs in a controlled manner such that the wt %Mn in solid solution is lower and at the same time the number of dispersoids is not increased [12].
2.6 Models for Microstructural Changes during Homogenization

Very few mathematical models have been developed to predict the microstructural evolution in an aluminum ingot as a function of time and temperature during homogenization. Only two models were found in the literature that had been developed to model microstructural changes during homogenization of AA3xxx aluminum alloys. A mathematical model is an attractive way to describe microstructural evolution, because the response of the microstructural features such as dispersoids and constituent particles to time, temperature and composition can be quantified.

To date, two researchers have attempted to model dispersoid formation during homogenization of AA3xxx alloys [34, 40].

Goodrich [34] used an Avrami type formulation (equation 3) to model the amount of Mn in solution for AA3104. The precipitation or dissolution rate constants in the model were dependent on temperature and the state of the preheat cycle and these were determined experimentally from isothermal treatments of an ingot. The fit was apparently quite good with Avrami exponents between 0.2-0.3.

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

where \( X \) is the fraction of Mn precipitated,

\( k \) is the rate constant,
t is the time in hours,

n is related to the type of reaction.

$X$ is expressed as:

$$X = \frac{C(t) - C_i}{C_e - C_i}$$  \hspace{1cm} (4)

Where: $C(t)$ is the dissolved Mn at any time $t$,

$C_i$ is the initial concentration of dissolved Mn,

$C_e$ is the "practical" Mn solubility for this alloy.

Goodrich's model was never validated using industrial measurements so it is difficult to comment on the accuracy of the predictions.

Suni [40, 41] developed a physically based model to predict the dispersoid evolution during homogenization of AA3003 and AA3004 aluminum alloys. His model combined the processes of nucleation, growth and coarsening so that particle size, density and volume fraction of dispersoids could be predicted. Model parameters were determined using industrial Alcoa data and the model predictions were then validated using industrial data and in general predicted sizes compared well to measurements.
2.7 Summary

Industrial can making is a complex process comprising various steps with many variable process parameters. Homogenization is the starting step in the processing of the ingot to the final sheet. It is important as the microstructure of the homogenized ingot can influence the strength, formability and the texture of the final gauge sheet for the canbody stock. Although studies have been completed over the past decade [10, 24, 25, 34] in an effort to understand the effect of the homogenization on the microstructural evolution, the ability to predict an optimum homogenization profile for a given starting structure and alloy composition has not yet been developed. Although some studies have been done investigating the effect of temperature and time of homogenization on the microstructures of AA3xxx aluminum alloys [21-26], there is almost no work studying the effect of heat-up rate. As such, there is no comprehensive study on the combined effect of the various homogenization parameters (heat-up rate, temperature, time, cool-down rate) on the microstructure evolution.
3. Scope and Objectives

3.1 Scope

The goal of homogenization process is not only to preheat the material to the desired hot rolling temperature but also allow segregated areas in the material to equilibrate. Currently in industrial practice, a wide variety of homogenization practices exist in terms of soak temperature, soak times and heat-up rate. In addition, newer cycles involving a second stage cool followed by a soak at a lower temperature have started to be investigated.

To date, a comprehensive study quantifying the effect of homogenization practice on the microstructural evolution has not been done. Such a study will be of benefit to aluminum sheet metal producers in that it will address the balance required in terms of developing the most economic practice in conjunction with one that obtains an optimum microstructure for hot rolling.

Although some studies have been done investigating the effect of temperature and time of homogenization on the microstructures of AA3xxx aluminum alloys [21, 26], there is almost no work studying the effect of heat-up rate. As such, there is no comprehensive study on the combined effect of the various homogenization parameters (heat-up rate, temperature, time). As a result, the purpose of this study was to examine various homogenization profiles and their effect of on the microstructural development during homogenization of an AA3104 aluminum alloy.
3.2 Objectives

The objectives of the present study are as follows:

i) to simulate typical industrial homogenization profiles in a laboratory furnace.

ii) to characterize the effect of homogenization process parameters on the microstructural evolution of aluminum alloy AA3104.
4. Experimental

4.1 Start Material

The experimental work was undertaken on an as-cast commercial AA3104 aluminum alloy. The material was received from Alcan International and was taken from an ingot that had been previously D.C. cast. The chemical composition of the alloy as supplied by Alcan and verified through low magnification EDX/SEM is shown in Table 4.1.

Table 4.1 - Composition of AA3104 alloy used.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg (wt%)</th>
<th>Mn (wt%)</th>
<th>Fe (wt%)</th>
<th>Si (wt%)</th>
<th>Cu (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA3104</td>
<td>1.20</td>
<td>0.87</td>
<td>0.40</td>
<td>0.20</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Microstructure and composition can vary dramatically across an ingot and the starting microstructure can greatly influence the microstructure evolution during homogenization [10, 11, 12]. To ensure homogeneity in the starting specimens, samples were cut 7-15cm from the ingot edge and were tested to ensure similar initial conductivity values. This ensured that conductivity (a measure of the amount of solute in solid solution) and cell size differences were minimized.
4.2 Homogenization Experiments

4.2.1 Laboratory furnace

The samples were homogenized in a programmable controlled laboratory furnace. To ensure accurate temperature control and homogeneity within the furnace, an aluminum tube was well fitted into the furnace with the controlling thermocouple inside the aluminum tube (Figure 4.1). Measurements of thermal profiles inside the modified furnace using instrumented samples indicated that the temperature variations were ± 2°C between the samples (Appendix A).

Figure 4.1 - Laboratory furnace set-up: a) overview and b) cross-sectional view.
4.2.2 Homogenization profiles

A wide range of homogenization profiles were simulated in the laboratory furnace so that the effect of heat-up rate, soak temperature, and soak time on the microstructural evolution could be quantified (Table 4.2).

Table 4.2 - Range of homogenization process parameters used in the study.

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat-up rate</td>
<td>37 - 279 °C/hr</td>
</tr>
<tr>
<td>Soak temperature</td>
<td>550 - 610 °C</td>
</tr>
<tr>
<td>Soak time</td>
<td>0 - 10 hrs</td>
</tr>
</tbody>
</table>

In addition, the effect of cool down to the rolling temperature after the homogenization treatment on the microstructure evolution was also studied.

Samples which were taken for microstructural characterization were quenched immediately from the homogenization cycle to ensure that the structure was representative of what is seen during homogenization. Figures 4.2-4.4 show the experimental homogenization cycles used as well as where samples were taken for microstructural characterization.
Figure 4.2 - Experimental homogenization profiles with varying heat-up rates (dots indicating where samples were taken for microstructure characterization).

Figure 4.3 - Experimental homogenization profiles with varying soak temperatures (550°C, 580°C and 610°C).
After an ingot is homogenized in industry, it cools down to the temperature at which hot rolling starts, also known as the lay-on temperature. Due to cool down, microstructural changes, especially in terms of Mn in solid solution are expected. Therefore, experiments that were conducted at different homogenization temperatures were cooled down to 500°C from the soak temperature in about half an hour (Figure 4.4).

In order to cool the samples down to 500°C, the furnace was turned off and the door was partially left open.

![Experimental thermal profiles used for samples homogenized at different soak temperatures.](image)

Figure 4.4 - Experimental thermal profiles used for samples homogenized at different soak temperatures.
4.3 Manganese Retained in Solid Solution

Electrical conductivity measurements were used to determine the amount of solute in solid solution. The sample conductivity was measured at 20°C as a percentage of International Annealed Copper Standard (%IACS) [18] using a Verimet 4900C eddy current probe. The readings (in %IACS) could then be directly used to estimate the %Mn in and out of solid solution. This is because Mg, a major alloying element, has a much lower effect on conductivity than Mn (Table 4.3) [18], almost all the Fe stays out of solution during the treatment, and Si and Cu levels in the alloy are too low to significantly affect the conductivity readings. Resistivity values could be obtained from conductivity measurements by the simple equation [42]:

$$\rho = \frac{172.41}{(%IACS)}$$

(5)

where \(\rho\) is resistivity in \(\mu\Omega\text{cm}\). Conversion of resistivity values to wt.% Mn in solid solution can then be done using the graph shown in Figure 4.6 [43].

<table>
<thead>
<tr>
<th>Element</th>
<th>AA3104 composition (wt%)</th>
<th>Average increase in resistivity per wt% in solution ((\mu\Omega\text{cm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.87</td>
<td>2.94</td>
</tr>
<tr>
<td>Mg</td>
<td>1.20</td>
<td>0.54</td>
</tr>
<tr>
<td>Fe</td>
<td>0.4</td>
<td>2.56</td>
</tr>
<tr>
<td>Si</td>
<td>0.2</td>
<td>1.02</td>
</tr>
</tbody>
</table>
Figure 4.6 - Resistivity of aluminum alloy 3004 as a function of the percentage of Mn in solid solution [43].

4.4 Microstructure Characterization / Metallography

4.4.1 Grinding and Polishing Procedure

Samples were cold mounted in an epoxy resin. All samples were polished using the Buehler Ecomet IV Polisher/Grinder which is a ten mount automatic polisher. The following schedule (Table 4.4) was standardised after trial and error and consultation with Tech-Met Canada:
Table 4.4 - Grinding and polishing procedure followed.

<table>
<thead>
<tr>
<th>Abrasive type</th>
<th>Abrasive Size</th>
<th>Lubricant</th>
<th>Pressure (psi)</th>
<th>Time (min)</th>
<th>Additional comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC paper</td>
<td>180 grit</td>
<td>Water</td>
<td>20</td>
<td>2</td>
<td>Repeated step till surface was flat</td>
</tr>
<tr>
<td>SiC paper</td>
<td>320 grit</td>
<td>Water</td>
<td>40</td>
<td>2</td>
<td>Changed paper after 1 min if murkiness not noticed</td>
</tr>
<tr>
<td>Diamond suspension on</td>
<td>6µm</td>
<td>Metadi fluid</td>
<td>40</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Texmet 1000 cloth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamond suspension on</td>
<td>1µm</td>
<td>Metadi fluid</td>
<td>40</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Texmet 1000 cloth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colloidal SiO₂ suspension</td>
<td>0.05µm</td>
<td></td>
<td>30</td>
<td>2</td>
<td>Washed with water for last 10 secs</td>
</tr>
</tbody>
</table>

4.4.2 Etching

The chemical etchant selected had to adequately distinguish between the two predominant constituent phases namely α-Al₁₂(Fe,Mn)₃Si and Al₆(Fe,Mn). From literature, two etchants were found to do this, 10% H₃PO₄ at 20°C [16], and H₂SO₄ at 80°C [12]. H₃PO₄ was tried and found to distinguish the two phases adequately for image analysis. Quantification of dispersoids was also attempted, and H₃PO₄ was effective in a qualitative viewing of dispersoids. 0.5% HF, an etchant used in literature [18] was also tried but was unsuccessful.
Samples were etched with 10% $\text{H}_3\text{PO}_4$ for 8 minutes at room temperature to distinguish between the second phases ($\alpha$-$\text{Al}_{12}($Fe,Mn$)_3\text{Si}$ and $\text{Al}_6($Fe,Mn$)$). The $\alpha$-$\text{Al}_{12}($Fe,Mn$)_3\text{Si}$ etched considerably darker while $\text{Al}_6($Fe,Mn$)$ was grey when viewed optically (Figure 4.7). The differentiation was confirmed by analysis using EDX/SEM (Figure 4.8) where only the darker particle showed a Si peak confirming it to be $\alpha$-$\text{Al}_{12}($Fe,Mn$)_3\text{Si}$.

Figure 4.7 - As-cast microstructure (1000X) showing the various second phase particles.
a) Particle etched black showing Al, Si, Mn and Fe peaks.

b) Particle etched grey showing Al, Mn and Fe peaks.

Figure 4.8 – EDX/SEM results confirming the etching difference between $\alpha$-$\text{Al}_{12}($Fe,Mn)$_3\text{Si}$ and $\alpha$-$\text{Al}_6($Fe,Mn) particle.
4.4.3 Electron Probe Micro Analysis (EPMA) Line Scans

It is known that the as-cast microstructure has microsegregation of eutectic elements such as Mg and Mn, which is eliminated during homogenization. To find out the temperature at which Mg and/or Mn diffuses so that microsegregation is reduced across the cell during homogenization, EPMA line scans were taken using the Scanning Electron Microscopy coupled with WDX.

4.4.4 Image Analysis

Quantitative metallography was done on a C-Imaging Systems optical image analyzer. The coarse eutectic intermetallic particles were analyzed at (32X) objective magnification whereas the dispersoids were distinguished at (50X) objective magnification. As there was a lot of microsegregation seen in the as-cast and partially homogenized samples, data was collected over a large number of fields till the cumulative averages of the data collected stabilized as shown in Figure 4.9. For the coarse constituent particles, data was collected from 40 to 80 fields depending on how quickly the average stabilized, with the stabilized average being used for subsequent analysis. Even so, due to the high variations in the readings between individual fields, the standard error was quite large.
Figure 4.9 - Variation of the cumulative average per field with the measured quantity per field for volume fraction second phase.

4.5 As-Cast Characterization

Initial material characterization involved quantifying the as-cast microstructure and manganese (Mn) retained in solid solution. Due to the large variances in as-cast microstructure (cell size and microsegregation) reported in the literature, samples were chosen from 5 to 25 cm from the surface of the ingot to minimize differences in the starting composition and microstructure. Table 4.5 gives the as-cast characterization in terms of wt% Mn in solid solution converted from conductivity measurements and second phase quantification.
Table 4.5 - As-cast characterization between 5 - 25 cm from surface.

<table>
<thead>
<tr>
<th>Wt.% Mn in solid solution</th>
<th>Second phase Vol. Fraction (%)</th>
<th>$\alpha$-$\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ (% second phase)</th>
<th>$\text{Mg}_2\text{Si}$ (% second phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66</td>
<td>2.75</td>
<td>~16</td>
<td>~11</td>
</tr>
</tbody>
</table>

Total second phase volume fraction included $\alpha$-$\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$, $\text{Al}_6(\text{Fe},\text{Mn})$ and $\text{Mg}_2\text{Si}$ (Figure 4.7). The majority of the second phase comprised of $\text{Al}_6(\text{Fe},\text{Mn})$ which amounted to about 73% of the total second phase. The $\text{Mg}_2\text{Si}$ was seen as a dark agglomeration of circular particles. The $\alpha$-$\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ also etched dark and was usually present as part of the eutectic interdendritic structure. The $\text{Al}_6(\text{Fe},\text{Mn})$ phase and was grey when viewed optically.
5. Results and Discussion

The experimental results of this study are outlined in this section, describing the qualitative and quantitative effect of process parameters on the microstructural evolution during homogenization. The effect of the homogenization cycle on the final sheet properties in terms of microstructure and texture are also described.

5.1 Microstructure Evolution during Homogenization

The effect of homogenization cycle on the microstructural evolution was assessed varying process parameters such as heat-up rate, soak temperature and soak time, and characterizing the microstructure of the samples at various points in the homogenization cycle. Microstructure evolution during the homogenization cycle was characterized by conductivity measurements (to assess the %Mn in solid solution) as well as image analysis to quantify the percentage of different constituent phases and examine the dispersoid distribution.

5.1.1 Effect of Heat-up Rate

The effect of heat-up rate to homogenization temperature on the microstructural evolution is described in this section in terms of:

- the %Mn in solid solution (Figure 5.1),
- the transformation of Al₆(Fe,Mn) to α-Al₁₂(Fe,Mn)₃Si (Figure 5.2),
- evolution of dispersoids(Figure 5.3) as well as,
- microsegregation.
5.1.1.1 Effect on Mn in Solid Solution

Mn being supersaturated in solid solution in the as-cast condition starts to come out as the temperature rises during heat-up. Depending on the heat-up rate, Mn precipitation is affected in terms of its initiation temperature and the amount that comes out (Figure 5.1). With increasing heat-up rate, Mn precipitation starts at a later temperature and less Mn precipitates out and dissolves back in during heat-up. In addition, the temperature at which the minimum level of %Mn in solid solution is found to increase as the heat-up rate is increased (Table 5.1).

![Figure 5.1 - Effect of heat-up rate on %Mn in solid solution.](image)
Table 5.1 - Minimum Mn in solid solution and corresponding temperature for different heat-up rates.

<table>
<thead>
<tr>
<th>Heat-up Rate (°C/hr)</th>
<th>Minimum %Mn in solid solution (wt %)</th>
<th>Temperature of minimum %Mn in solid solution (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>0.32</td>
<td>475</td>
</tr>
<tr>
<td>47</td>
<td>0.33</td>
<td>500</td>
</tr>
<tr>
<td>70</td>
<td>0.35</td>
<td>500</td>
</tr>
<tr>
<td>111</td>
<td>0.38</td>
<td>525</td>
</tr>
<tr>
<td>279</td>
<td>0.43</td>
<td>550</td>
</tr>
</tbody>
</table>

The following observations can be made from the results:

i) The temperature which attains the lowest Mn in solid solution (maximum precipitation rates) increases as heat-up rate increases ranging between 475°C and 550°C. This point corresponds to the rate of maximum precipitation rates [4, 16, 20]. As seen in the literature, the temperature of maximum precipitation rates for Mn is ~475°C. This corresponds to the temperature measured in our slowest heat-up rate of 37°C/hr.

ii) The amount of Mn that precipitates out of solid solution at the temperature of maximum precipitation rates decreases as the heat-up rate increases. This is expected based on the classical precipitation theory as a faster heat-up rate means there is less time at temperature to allow Mn precipitation.

iii) The total amount of Mn that precipitates out of solid solution at the end of the 3 hr hold at 580°C is almost identical for each heat-up rate. This was again expected since there was enough time during the soak period, to allow the precipitation of Mn into the
matrix until the equilibrium amount of Mn at the soak temperature was left in solid solution.

5.1.1.2 Constituent Particles and percent $\alpha$-Al$_{12}$(Fe,Mn)$_3$Si

The shape and size of the constituent particles was qualitatively observed after a three hour hold at the homogenization temperature of 580°C for each of the heat-up rate (Appendix B) and was not seen to be affected by the heat-up rate.

The Al$_6$(Fe,Mn) $\rightarrow$ Al$_{12}$(Fe,Mn)$_3$Si transformation was measured as percent $\alpha$-Al$_{12}$(Fe,Mn)$_3$Si of total second phase and plotted for a three hour hold at 580°C for the various heat-up rates (Figure 5.2). Although heat-up rates do not have a significant effect on percentage transformation, there is a trend showing a higher $\alpha$-phase at faster heat-up rates. Due to the high standard error during measurement, 95% confidence interval error bars suggest that no conclusive statement can be made about the increasing trend indicated on the graph.
Evolution of Dispersoids

Microstructures were taken from samples at a soak temperature of 580°C after a three hour hold for each of the heat-up rates (see Appendix B for a list of pictures for each profile). Dispersoids (seen as the fine dots in the microstructure) formed from a faster heat-up rate were larger and fewer than ones formed from a slower heat-up rate profile (Figure 5.3).
Figure 5.3 - Microstructures of samples for 580°C soak temperature after 3 hour hold for:

a) 279°C/hr and b) 47°C/hr.
Mn precipitates during heat-up in the form of $\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ dispersoids with the Mn precipitation kinetics bearing a direct relation to the dispersoid evolution [4, 19]. Since there has been no study on heat-up rate for AA 3xxx alloys, no results or theory was found in literature to confirm or explain these findings.

Evaluating %Mn in solid solution at specific temperatures during heat-up revealed that there was more precipitation in the 47°C/hr heat-up profile than the 279°C/hr profile (Figure 5.4). It was reasoned that due to the small time range during heat-up for the faster heat-up rate, the Mn precipitation rates were lower causing less dispersoids to nucleate. This was confirmed by the smaller minima of Mn in solid solution, as illustrated in Figure 5.1. The growth of the dispersoids, however, continued during the soak period and the fewer dispersoids grew larger with the available Mn in solid solution.
Figure 5.4 - Microstructures of samples at 450°C during heat-up for: a) 279°C/hr and b) 47°C/hr.
5.1.1.4 Removal of Microsegregation

Electron Probe Micro Analysis (EPMA) scans carried out on samples at various temperatures during heat-up showed that Mg and Mn microsegregation was removed from the samples at different temperatures (Table 5.2) (for micrographs see Appendix C). Mg microsegregation also referred to as Mg coring [33] is high in the as cast structure and is considerably reduced by the time the temperature reaches 500°C for the 47°C/hr profile and by 580°C for the 279°C/hr profile.

Table 5.2 - Mn and Mg segregation results for 47°C/hr and 279°C/hr profile at various temperatures during heat-up.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Heat-up profile 47°C/hr</th>
<th>Heat-up profile 279°C/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
<td>Mn</td>
</tr>
<tr>
<td>As-cast</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>400°C</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>500°C</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>580°C</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>580°C 3hr</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>
5.1.2 Effect of Soak Temperature and Soak Time

5.1.2.1 Effect on Mn in Solid Solution

As the soak temperature increases, the amount of Mn in solid solution at the soak temperature increases for both a fast (279°C/hr) and slow (47°C/hr) heat-up rate (Figure 5.5). This is in tune with the literature since Mn solubility increases with an increase in temperature [4, 26].

The effect of soak time at 550°C, 580°C and 610°C can also be estimated from Figure 5.5 for both heat-up rates. The results can be analyzed for two distinct regions:

i) Between 0 and 0.5 hrs - most profiles show an increase in the Mn in solid solution especially for the higher temperature profiles (580°C and 610°C). This could be attributed to the fact that at 0 hr hold even though the samples have reached the soak temperature the Mn re-dissolution kinetics are still catching up to reach the equilibrium amount of Mn in solid solution for that temperature.

ii) Between 0.5 hrs and 10 hrs: The results for this range show a slight drop in %Mn in solid solution with increasing soak time at higher soak temperatures (~600°C) whereas a steady amount or even a slight rise can be seen at lower soak temperatures (~550°C). The decrease in %Mn in solid solution during the soak period at higher homogenization temperatures have also been noted by other researchers [12, 19, 21]. The reason for this could be that at higher soak temperatures other processes competing for Mn become more favorable such as:
• $\text{Al}_6(\text{Fe,Mn}) \rightarrow \alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$: A higher $\%\alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ is reported at longer soak periods [4] (Figure 5.7) and there is a higher $\%\text{Mn}$ in $\alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ as compared to $\text{Al}_6(\text{Fe,Mn})$, and

• $\%\text{Mn}$ in constituent particles: A higher $\%\text{Mn}$ is seen in both $\alpha-\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ and $\text{Al}_6(\text{Fe,Mn})$ at higher soak temperatures [12, 26, 27].
Figure 5.5 - Mn in solid solution at different soak temperatures at a) 47°C/hr and b) 279°C/hr.
Constituent Particles and Percent $\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$

Particle coarsening occurs at high temperature hold during homogenization [10, 12, 24] with more coarsening at higher temperatures. However, in the present study, a significant coarsening was not observed in the particles. The particles at 610°C, however, were seen to be more rounded than at 550°C (Figure 5.8).

With higher soak temperatures, the $\text{Al}_6(\text{Fe,Mn})$ to $\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$ transformation is also enhanced such that the percentage of $\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$ is higher for higher soak temperatures (Figure 5.6). This trend is seen at both slow and fast heat-up rates with the total $\%\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$ being higher at the faster heat-up rates.

![Figure 5.6 - Effect of soak temperature on $\%\alpha$-$\text{Al}_12(\text{Fe,Mn})_3\text{Si}$ after a soak period of three hours.](image-url)
As the soak time is increased the percentage $\alpha$-phase increases and eventually levels off after a soak time of 3 hours is reached. The leveling was more pronounced for higher soak temperatures (Figure 5.7). This could be attributed to the unavailability of Mn due to higher Mn in solid solution at the end of 10 hrs for the higher soak temperature (Figure 5.5).

Figure 5.7 - Effect of soak time on $\%\alpha$-$\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ at various soak temperatures at a heat-up rate of $47^\circ\text{C/hr}$. 

63
5.1.2.3 Evolution of Dispersoids

The effect of soak temperature on the evolution of dispersoids can be estimated qualitatively from the microstructure inspection of samples from 550°C, 580°C and 610°C soak temperature after three hour hold with a heat-up rate of 47°C/hr (Figure 5.8). The dispersoids at 550°C are smaller and more in number, the number decreasing and the size increasing with an increase in the soak temperature till at 610°C there are very few dispersoids observed, and the ones present are very coarse. There are two main mechanisms that contribute to the observed results:

i) Growth of dispersoids is a diffusion-based process and as temperature rises from 550° to 610°C, the rates of this process increase rapidly.

ii) Increased solubility of Mn at higher temperatures lead to a dissolution of the smaller dispersoids into the matrix thereby explaining the low number of dispersoids seen in the sample which had been homogenized at 610°C.
a) 550°C

b) 580°C
c) 610°C

Figure 5.8 - Microstructures (1000X) of samples after three hour hold with a heat-up rate of 47°C/hr for soak temperatures of: a) 550°C, b) 580°C and c) 610°C.

5.1.2.4 Cool Down to Rolling Temperature

The effect of soak temperature is seen to translate to a difference in %Mn in solid solution even when the samples were cooled down to a similar temperature of 500°C (Figure 5.9), with the samples which had been soaked at a higher temperature exhibiting a higher level of Mn in solid solution.
Figure 5.9 - Mn in solid solution for homogenization profiles of 550°C, 580°C and 610°C for three hour hold followed by cool down to 500°C.

During cool down, very little change takes place in the morphology or size of the constituent particles, the precipitating Mn comes out enlarging the pre-existing dispersoids (Figure 5.10). Hence, the higher number of dispersoids in the 550°C sample (Figure 5.8) are also carried forward at the end of the cool down to 500°C.
Figure 5.10 - Microstructures (1000X) of samples after a cool down to 500°C for soak temperatures of: a) 550°C, b) 580°C and c) 610°C.
5.2 Influence of Homogenization Microstructure on Texture/Microstructure after Hot-Rolling

The size and shape of the constituent and dispersoid phases formed in the ingot during homogenization influence the size distribution of the second phases in the final gauge sheet [4, 12, 37, 45, 46] as well as the recrystallization kinetics and texture formation after hot rolling. During hot rolling, the eutectic networks of constituents break down and depending on the rolling temperature, recrystallization of the grains initiates during/after rolling [11, 12, 48]. The morphology and size distribution of the constituent particles (α-Al_{12}(Fe,Mn)_{3}Si and Al_{6}(Fe,Mn)) affects the cube texture evolution due to particle-stimulated nucleation (PSN) during recrystallization after hot-rolling, die-cleaning during ironing in the bodymaker operation, and tear-off tendency [4, 12, 45, 48, 47]. The dispersoids, on the other hand, affect the texture by retarding recrystallization [45, 46, 48].

The morphology of the constituent particles in terms of the percent α-Al_{12}(Fe,Mn)_{3}Si phase determines the die-cleaning efficiency of the alloy during drawing. The constituent α-Al_{12}(Fe,Mn)_{3}Si phase is relatively harder (Vickers micro-hardness of 900-950 Hv) than the Al_{6}(Fe,Mn) phase, which has hardness of 700-750 Hv [4, 16, 22]. Hence a certain fraction (greater than 40%) of α-Al_{12}(Fe,Mn)_{3}Si constituent particles is desirable for prevention of galling (the seizure of metal on the working surfaces of the dies observed when the constituent particles are not hard enough). The majority of the
manufacturers in the industry control the percent $\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ phase fraction between 50 and 60% [23].

To minimize earing during the can drawing operation, adequate amounts of cube texture ($0/90^\circ$ ears) are needed after hot rolling. However, large constituent particles can cause deformation zones to form around them during hot rolling, and during subsequent annealing, these deformed zones become nucleation sites for recrystallization. PSN results in random texture, which reduces the effective cube content, and hence decreases the cube texture in the final gauge sheet [45, 5]. Hence, it is not favorable to have a large number of constituent particles.

Mn retained in solid solution retards recrystallization during annealing after hot rolling [12]. It is desired to achieve a totally recrystallized microstructure before the final cold roll step to obtain a sufficient amount of cube texture [39]. Hence, it is desirable to have as low a %Mn in solid solution after hot rolling as possible.

The number and size distribution of dispersoids that evolve during homogenization are important parameters in determining the amount of cube texture formed. These dispersoids exert a retarding force on the low/high angle grain boundary, which can affect the kinetics of recovery, recrystallization and grain growth. This effect is known as Zener drag [45] and can be expressed as:

$$P_z = \frac{(3F_v \gamma)}{2r} \quad (6)$$

Where $F_v$ is the volume fraction of randomly distributed spherical particles of radius $r$, and $\gamma$ is the grain boundary energy reported to be 324 mJ/m$^2$ [49] for aluminium. From equation (6) it can be deduced that the Zener drag is a function of volume fraction
(Fv) and size r (radius) of the dispersoids such that a large volume fraction of small dispersoids increases Zener drag.
6. Summary and Conclusions

During the manufacturing of aluminum beverage cans from the ingot through the cold rolled sheet, it is important to control the microstructure and texture evolution as they will control the final mechanical properties and performance of the alloy during the can making operation. Since the homogenization profile the ingot undergoes, will influence the starting microstructure prior to hot rolling, it is critical to characterize and quantify the influence of various homogenization parameters on the microstructure evolution and determine the "optimum" homogenized microstructure.

6.1 Summary

The present research was primarily concerned with characterizing and quantifying the effect of homogenization process parameters on the microstructural evolution of an AA3104 aluminum alloy. The following observations can be made based on the study:

i) Heat-up rate to the soak temperature affected the amount of Mn precipitating out and re-dissolving in solid solution during heat up. However, the total amount of Mn that precipitated out of solid solution at the end of three hours at the soak temperature was almost identical for each heat-up rate. The variation in Mn during heat-up affected the size and shape of the evolving dispersoids; the dispersoids became fewer and appeared coarser as the heat-up rate increased possibly due to the lower amount of Mn precipitation during heat-up. The shape and size of the constituent particles was not
affected by the heat-up rate, but there was a slight increase in the percent $\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ seen for the faster heat-up rates. This may have occurred because of the extra Mn that was available due to fewer dispersoids. An increase in heat-up rate also caused a delay in reduction of Mg and Mn microsegregation across the cell.

ii) As soak temperature was increased, the amount of Mn in solid solution increased for each heat-up rate. The rise in Mn in solid solution was accompanied in parallel by a drop in dispersoids. Higher soak temperatures also resulted in a higher $\%\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ particles.

iii) Increasing soak times also increased the $\%\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ initially but started tapering off for longer soak times of 3 hrs as the equilibrium amount of $\%\alpha$-$\text{Al}_{12}(\text{Fe,Mn})_3\text{Si}$ was approached for the soak temperature. Higher soak temperature profiles tapered faster due to the lower amount of Mn in solid solution. Mn in solid solution was affected inversely with increasing soak times. A drop was seen in $\%\text{Mn}$ in solid solution with increasing soak times between 0.5 to 3 hrs. Between 0 and 0.5 hrs the Mn level still increased in all profiles due to lag in Mn dissolution kinetics to reach the equilibrium amount of Mn for that soak temperature. Dispersoids on the other hand, were qualitatively assessed to have coarsened slightly without a noticeable increase in their number.

Since the microstructure after the homogenization process will influence the microstructure and sheet properties that develop during and after hot rolling, it is important to understand the influence of key microstructure features on the both the microstructure evolution during hot rolling as well as the final material properties. A summary of desired microstructure characteristics after homogenization include
• a fair amount of α-Al_{12}(Fe,Mn)_{3}Si preferably over 50% and definitely not below 40% (to minimize galling),

• minimum coarsening of the constituent particles so as to obtain a minimum number of large constituent particles after hot rolling (particles greater than 1-2μm promote PSN during recrystallization [12]),

• a small volume fraction of dispersoids which are as large as possible so as to minimize the Zener drag effect which can inhibit recrystallization and thereby lower the total amount of cube texture after hot rolling, and

• low %Mn in solid solution after hot rolling so that the temperature at which recrystallization occurs is not too high and the material can self-anneal during coiling.

6.2 Conclusions

From the results, the following conclusions can be made for a suitable homogenization profile:

• A faster heat-up rate is more favorable in terms of the formation of fewer dispersoids and a slightly higher volume fraction of α-Al_{12}(Fe,Mn)_{3}Si.

• A soak temperature of 610°C is preferred as it achieves the required volume fraction of α-Al_{12}(Fe,Mn)_{3}Si and leads to a lower volume fraction of dispersoids with a larger size. The disadvantage of a higher soak temperature is that there will be a higher level of Mn in solid solution during hot rolling which could inhibit recrystallization during
annealing after hot rolling. However, this could be lowered before annealing by adjusting the rolling temperatures.

- Soak times at temperature allowed the $\%\alpha\text{-Al}_{12}(\text{Fe,Mn})_3\text{Si}$ to increase (~15% from 0 to 3 hours), however, given a high soak temperature, high soak times could increase the size of the constituent particles promoting PSN. Beyond three hours there did not appear to be much change in the microstructure even for the material heated using a fast heat-up rate.

Based on this study, it appears that for an AA3104 alloy used for canbody stock the optimum homogenization profile includes: a fast heat-up rate to a high homogenization temperature ($580^\circ\text{C} - 610^\circ\text{C}$) with moderate soak times (0.5-3 hrs).

Other conclusions that can be drawn from the study are:

i) There is a significant difference in the microstructure obtained between the industrial standard heat-up rate range ($45^\circ\text{C/hr} - 70^\circ\text{C/hr}$) profile and very fast heat-up rates. Hence, in order to apply laboratory based homogenization results, it is critical that similar heat-up rates to industrial conditions be applied to the samples (i.e., samples which have been heated using salt baths would give very different microstructures than the ones industrially heated even if they have been held at $580^\circ\text{C}$ for 3 hrs.)

ii) Even though the heat-up rate had a significant impact on the microstructure evolution, within the current industrial heat-up rate range (i.e., soaking pits (~$50^\circ\text{C/hr}$) Vs. walking beam furnaces (~$70^\circ\text{C/hr}$)), there is not a significant difference in the microstructure obtained.
6.3 Future Work

Based on this study, the following are some of the topics that may be considered for future work:

i) Quantification of dispersoids was not possible with optical image analysis or SEM. Hence, TEM analysis of multiple fields within samples in each profile is recommended to complete quantification and numerical analysis of microstructure evolution during homogenization.

ii) One of the interesting observations in this study was the lowering of Mn in solid solution with time at higher temperatures. To explain the results and validate the theory proposed extensive fundamental research is required studying the thermodynamic relationship between Mn in solid solution, $\text{Al}_6(\text{Fe},\text{Mn}) \rightarrow \alpha-\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$ transformation and Mn in $\text{Al}_6(\text{Fe},\text{Mn})$ and $\alpha-\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si}$.

There is very little literature available covering the thermodynamics involved in the AA3104 alloys. To the best of the author's knowledge the Al-Mg-Mn-Fe-Si phase diagram is not yet known; it is under investigation in the European COST 507 (CO-operation in Science and Technology) action [50, 51, 52].

iii) Finally, modeling the microstructure evolution would be a useful undertaking especially if the thermodynamic data is available. The model would predict the microstructure characteristics given homogenization process parameters. The model could be tested against the results obtained in this study.
Bibliography


35. Private communication with Alcan International.


44. Tromberg E., Dons A.D., Amber L., "Investigation of the \( \text{Al}_6(\text{Fe},\text{Mn}) \rightarrow \alpha-\text{Al}_{12}(\text{Fe},\text{Mn})_3\text{Si} \) phase transformation during homogenization of AA3003 and AA3004 Aluminum Alloys", The 3rd International Conference of Aluminium Alloys, 1992, 270-275.


Appendix A

Temperature profile of aluminum samples in original and retrofitted (i.e. with aluminum tube) furnace.
Figure A1 - Temperature variations between furnace (580°C) and sample of original furnace at a) two sample positions in the furnace, and b) on a raised platform near the furnace thermocouple.
Figure A2 - Temperature variations between furnace (580°C) and sample temperature in the retrofitted furnace.
Appendix B

Microstructures of samples heated to 580°C using different heat-up rates and held for three hours:
a) 37°C/hr

b) 47°C/hr
c) 70°C/hr

d) 112°C/hr
Figure B1 - Microstructures of samples at 580°C soak temperature after 3 hr hold for a) 37°C/hr, b) 47°C/hr, c) 70°C/hr, d) 112°C/hr, and e) 279°C/hr.
Appendix C

EPMA line scans (Mg and Mn) at various temperatures during heat-up to 580°C using two different heat-up rates (47°C/hr and 279°C/hr).
Figure C1 – EPMA line scans (Mg and Mn) for the as-cast microstructure.
Figure C2 - EPMA line scans (Mg and Mn) for 47°C/hr profile at a) 400°C, b) 500°C, 580°C (0 hrs), and d) 580°C (3hrs).
a) 400°C

b) 500°C
Figure C3 - EPMA line scans (Mg and Mn) for 279°C/hr profile at a) 400°C, b) 500°C, 580°C (0 hrs), and d) 580°C (3 hrs).