DEVELOPMENT OF NOVEL GRAIN REFINERS FOR AZ91D MAGNESIUM ALLOYS

AND THEIR EFFECT ON HOT TEARING

by

Tyler Alexander Davis

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The following individuals certify that they have read, and recommend to the College of Graduate Studies for acceptance, a thesis/dissertation entitled:

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submitted by Tyler Alexander Davis in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Mechanical Engineering.

Dr. Lukas Bichler, School of Engineering

Supervisor
Dr. Dimitry Sediako, School of Engineering

Supervisory Committee Member
Dr. Jian Liu, School of Engineering

Supervisory Committee Member
Dr. David Jack, Irving K. Barber School of Arts and Sciences

University Examiner
Dr. Sumanth Shankar, McMaster University, Faculty of Engineering

External Examiner
Abstract

Wider implementation of ultralight magnesium (Mg) alloys in engineering applications can be achieved if the mechanical properties of mass produced as-cast alloys can be further enhanced. Grain refinement of aluminum alloys has supported such initiatives over the past few decades; however, a potent and cost-effective grain refiner for common aluminum containing Mg alloys remains elusive. Further, the effect of grain refinement on common casting defects, such as hot tearing, in Mg alloys remains unclear.

In this work, several novel grain refiners were produced via the powder metallurgical process known as spark plasma sintering (SPS). The novel grain refiners were used to treat AZ91D Mg alloy and a grain size reduction of ~75 - 85% was achieved, along with improved dispersion of secondary phases and modified eutectics. Such microstructure modifications during solidification resulted in the elimination of hot tearing in castings where hot tearing was typically observed. The SPS’ed refiners were also observed to outperform a common commercially available grain refiner.

Many advanced analysis techniques that were implemented in this research provided further understanding of the mechanism behind the effectiveness of the SPS’ed grain refiners. Additionally, the casting experiments were completed using a unique force contraction mold, providing quantitative data during solidification. Furthermore, the results of microstructure evolution, solidification kinetics and forces, as well as in-situ solidification analysis via neutron diffraction, was related to the grain refinement and hot tearing of AZ91D Mg alloy.
Lay Summary

With climate change on the rise, a reduction in fuel emissions is required. This can be achieved through weight reductions of cast components in automotive and aerospace vehicles. Magnesium (Mg) and its alloys have been sought out as they are ~80% lighter than steels and ~30% lighter than aluminum. Unfortunately, Mg alloys commonly have poor as-cast properties and a high susceptibility to casting defects, limiting the application of cast Mg alloys in industry. Using unique grain refinement additives developed with powder metallurgy, improvements to the microstructure and defect resistance was observed. Using advanced analysis techniques, the unique additives’ effect on the solidification process was further analyzed to shed light on the exact mechanisms at hand.
Preface

This dissertation titled “Novel Grain Refinement of Magnesium Alloys and the Effect on Hot Tearing” was written in the fulfillment of the degree, Doctor of Philosophy (Ph. D) in Mechanical Engineering, at the University of British Columbia.

The author and collaborators contribution to the research presented in this dissertation is as follows: Initial construction and testing of the unique casting setup was completed by Tyler Alexander Davis with supervision by Dr. Lukas Bichler. Support and advice were provided by Dr. Norbert Hort, and Dr. Francesco D’Elia, who originally supplied the steel hot tear mold, from the Magnesium Innovation Centre at Helmholtz-Zentrum-Geesthacht, Germany.

Development of the Spark Plasma Sintered grain refiners was completed by Tyler Alexander Davis with supervision by Dr. Lukas Bichler and Mr. Anil Prasad. All metal casting experiments were conducted by Tyler Alexander Davis with the assistance of Mr. Justin Mok, Dr. Lukas Bichler, Mr. Levi Lafortune and Mr. Anil Prasad. All sample preparation for subsequent analysis was completed by Tyler Alexander Davis with instruction from Dr. Lukas Bichler. All optical microscopy was completed Tyler Alexander Davis with advice from Dr. Lukas Bichler and assistance from Ms. Somi Doja. Scanning Electron Microscopy was completed at the Charles Fipke Particle Research Centre with supervision and assistance from Mr. David Arkinstall. X-ray Diffraction experiments were completed at the University of British Columbia’s Chemistry Department in Vancouver, BC by Ms. Anita Lam. Analysis of X-ray Diffraction data was completed by Tyler Alexander Davis with assistance from Mr. Anil Prasad. Electron Back Scatter analysis was completed by Tyler Alexander Davis with supervision and assistance from Mr. David Arkinstall at the Charles Fipke Particle Research Centre. Neutron Diffraction experiments were completed by Dr. Dimitry Sediako and Tyler Alexander Davis at the Canadian Nuclear Laboratories at the Canadian Neutron Beam Centre in Chalk River, On. Subsequent analysis of the unique Neutron Diffraction data was
completed by Tyler Alexander Davis with direct instruction from Dr. Dimitry Sediako.

Analysis of the hot tearing and in-situ data collected was analyzed by Tyler Alexander Davis with assistance and advice from Dr. Lukas Bichler. Additionally, support and advice were given by Dr. Norbert Hort, and Dr. Francesco D’Elia from the Magnesium Innovation Centre at Helmholtz-Zentrum-Geesthacht, Germany.

The Introduction, Literature Review, and Experimental Procedure were written by the author independently. Advice and recommendations were provided by the supervisor, Dr. Lukas Bichler. The Results and Discussion were written independently by Tyler Alexander Davis with advice from Dr. Lukas Bichler. Instruction and guidance were provided by Dr. Dimitry Sediako on Sections related to Neutron Diffraction and Mg alloys. Several Sections of the results were complied into several manuscripts; below is the list of currently published and planned journal papers. Additionally, several conference presentations were completed.


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To the ones I love
and those who have
supported me
throughout
Chapter 1: Introduction

During the past few decades, the automotive and aerospace industries have intensified efforts to reduce harmful emissions, such as CO$_2$ and NO$_x$ originating from vehicles and aircraft. One method of achieving this goal is by reducing the weight of vehicles or aircraft. As a result, with magnesium (Mg) being one of the lightest structural metals currently used in engineering applications. In particular, the application of Mg and its alloys for the transportation industries continues to be extensively studied globally [1], [2], [3], [4]. Mg alloys are ~30% lighter than aluminum (Al) alloys and ~80% lighter than Steel [1], [2], [5], [6], which makes the specific properties of Mg alloys highly attractive for many industrial applications. Also, Mg alloys have a lower reactivity with steel molds as compared to Al alloys, resulting in steel casting molds lasting 3 - 4x longer with Mg alloys. Unfortunately, however, Mg alloys are susceptible to several casting defects, such as porosity and hot tearing, which continue to hinder a wider adaptation of Mg alloys in the transportation industries [3], [4], [7], [8], [9].

Hot tearing is a metal casting defect that occurs during the late stages of solidification [7], [10], [11], [12], [13], [14]. A permanent crack (i.e., a hot tear) forms as a result of inadequately controlled solidification shrinkage. In a geometrically constrained casting configuration, the solidification shrinkage causes stress and strain to develop in the casting [6], [14], [15]. With progressing solidification, a hot tear can form if the interdendritic structure is unable to sustain the solidification stress and or the strain [13], [14], [16], [17].

The reduction or elimination of hot tears has been primarily achieved by reducing the alloy’s cooling rate during solidification [17], [18], [19], [20], [21]. The cooling rate can be controlled by preheating the casting mold to at least ~50-70 °C below the solidus temperature of the alloy, which is energy intensive [9], [22]. Such hot molds and slow cooling tend to produce castings with a large grain structure, resulting in poor mechanical performance. Therefore,
alternatives to cooling rate manipulation have been explored, and the use of grain refinement during solidification shows promising opportunities [8], [16], [21]. Grain refinement is a process where inoculant particles are added to the molten metal prior to casting in order to reduce the grain size of the alloy. The particles act as heterogeneous nucleation sites and promote rapid and homogeneous grain formation throughout the casting. However, the key to effective grain refinement is the uniform distribution of the refining particles in the liquid metal.

In the present work, a novel method of introducing grain refining particles into liquid AZ91D Mg alloy was developed. A powder metallurgy process called Spark Plasma Sintering (SPS) was used to fabricate novel grain refiners. A homogenous blend of refining particles and matrix powder was sintered into a solid pellet. This solid pellet was then added into the liquid AZ91D Mg alloy prior to making a casting. Once immersed in the melt, the matrix of the SPS’ed pellet dissolved and released the refining particles uniformly in the liquid AZ91D Mg alloy.

To quantify the effect of grain refinement on hot tearing, a horizontal constrained rod casting (CRC) mold instrumented with a load cell was used. The mold was extensively tested by several researchers [14], [17], [23]. The CRC mold was specially designed to isolate and quantify hot tearing during casting solidification.

In addition to the CRC tests, the grain refined AZ91D Mg alloy castings were characterized with diverse methods. In-situ Neutron Diffraction (ND) during alloy solidification of the grain refined alloy was used to examine the effect of the novel grain refiners on the solidification kinetics. Electron Back Scatter Diffraction (EBSD) mapping of the grain structure near the critical hot tear region was completed to study texture and grain alignment. Other analysis techniques used included X-Ray Diffraction (XRD) for phase analysis, Scanning Electron Microscopy (SEM) for high magnification microstructure analysis, X-ray Energy Dispersive
Spectroscopy (XEDS) for chemical analysis, and optical microscopy (OM) for grain size analysis.

The goal of this research was to carry out a comprehensive quantitative analysis of the effect of grain refinement on the microstructure of the AZ91D Mg alloy, as summarized in Figure 1-1. In addition, the effect of grain refinement on the alloy’s hot tearing susceptibility was studied. As a result, the objectives of this research were:

1. Constructing, calibrating and testing the CRC mold for AZ91D Mg alloys.
2. Determining the casting parameters related to the onset of hot tearing of the AZ91D Mg alloy.
3. Developing novel Al-Ti-B, Al-Ti-C, Al-C and Al-Ti grain refiners via SPS.
4. Refining the AZ91D Mg alloy with the novel refiners at two different mold temperatures.
5. Quantifying the hot tear severity and as-cast microstructure with respect to the different grain refiners.
6. Relating in-situ solidification data from casting experiments to the hot tear severity.
7. Studying the solidification kinetics of refined castings through ND.
Figure 1-1: Research overview.
Chapter 2: Literature Review

This chapter provides a concise review of literature relevant to this dissertation. A general overview of magnesium alloys, as well as theories pertinent to alloy solidification, hot tearing and grain refinement are critically discussed.

2.1 Magnesium and Magnesium Alloys

Mg and its alloys have a density of ~1.74 g/cm³, which makes them one of the lightest structural metals with excellent strength to weight ratio [1], [2], [3], [4]. Also, Mg alloys have a good castability, recyclability and optimal energy damping capacity, which makes them desirable for many automotive components [1], [2], [3], [4], [5]. Mg alloy solid solutions, much like other alloy systems, were developed with consideration of the Hume-Rothery rules [4], [5]. The four rules that determine a solute’s ability to dissolve into a solvent matrix are:

1. Atomic size factor: the diameter of the solute and solvent atoms must be within ±15%.

2. Crystal structure: the solute and solvent should have a matching crystal structure [5].

3. Electronegativity: if the solute and solvent have a large difference in electronegativity, they will have a better chance of forming an intermetallic compound instead of a solid solution [5].

4. Valency: a solute will have a better chance of dissolving in a solvent with a higher valency [5].

For industrial applications, Mg alloys are classified based on whether the alloys contain Al. Al-free Mg alloys are most often used in specialty castings, with the zinc-zirconium (ZK) series of Mg alloys being prominent due to their excellent strength and corrosion resistance [3], [24], [25], [26], [27]. Zinc-rare earth (ZE) series Mg alloys are made for applications
where creep resistance and improved strength are required [1], [2]. Yttrium-rare earth (WE) series Mg alloys are used in high temperature applications, since both Y and RE improve the creep resistance and high temperature strength of Mg [4], [27], [28]; however, the WE alloys are often costly, and thus their applications remain limited.

The Hume-Rothery rules were extensively used when developing Mg alloys with Al as a solute, due to the close matching of atomic sizes and electronegativities. The Mg-Al alloy systems represent the majority of industry-relevant Mg alloys currently in use [3], [4]. The ability to alloy Al into Mg is based on the similarity of atomic radii between Mg and Al (~0.17 nm and ~0.14 nm, respectively) [5]. Also, the crystal structure of Mg is Hexagonal Close Packed (HCP), while that of Al is Face Centered Cubic (FCC). However, their close-packed plane stacking sequence makes their crystal structures amenable for bonding [4], [5], [29]. Mg and Al also have similar electronegativities and valences.

### 2.1.1 Aluminum Containing Mg Alloys

Al containing Mg alloys often contain Zinc (Zn), Manganese (Mn), Rare Earths (RE), Strontium (Sr) and Silicon (Si) as secondary alloying elements. These elements manipulate the alloy strength at low or high temperature, alloy fluidity, and corrosion resistance [1], [2], [3].

The most common Mg-Al magnesium alloy family is represented by the AZ91 Mg alloy, with ~9wt% Al and ~1 wt% Zn as primary alloying elements [3], and secondary elements in trace quantities (Table 2-1). The non-equilibrium liquidus and solidus temperatures were used for solidification analyses which were ~595 °C and ~437 °C, respectively, for the AZ91D Mg alloy [1], [2], [5], [30]. Equilibrium cooling assumes solid and liquid exist in equilibrium at every temperature. This requires slow cooling rates, which are often not practical. [5]. In contrast, non-equilibrium cooling calculations (used throughout this thesis) consider the rate at which the alloy cools from the actual liquidus to the actual solidus temperature. Figure 2-1
shows the Mg-Al phase diagram which is often used in reference for Mg-Al magnesium alloys.

Table 2-1: Nominal composition of AZ91D Mg Alloy (wt%) [1], [2].

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.3-9.3</td>
<td>0.6-1.0</td>
<td>0.13-0.22</td>
<td>&lt;0.035</td>
<td>&lt;0.005</td>
<td>&lt;0.003</td>
<td>&lt;0.002</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Figure 2-1: Mg-Al binary phase diagram [1].

The primary alloying elements, Al and Zn, are added to improve the strength and corrosion resistance of the Mg solid solution [1], [2], [5], [31]. The Al content of ~9wt% was determined to impart an optimum strength for the AZ series alloys. However, when the Zn content exceeds ~1-2wt% in Mg alloys with high Al content (i.e., 9wt%), additional phases readily form (e.g., Mg\textsubscript{32}(Al, Zn)\textsubscript{49}), and increase defect susceptibility during manufacturing operations (i.e., porosity and/or hot tearing) [2], [4]. Silicon (Si), Iron (Fe), Copper (Cu), and
Nickel (Ni) may be present in the AZ91D Mg alloy as impurities, since these elements increase the corrosion susceptibility of the alloy, and thus their concentration must be carefully monitored [1], [2].

2.2 Grain Refinement

Solidification represents the transformation of liquid metal to a solid state. In pure metals under equilibrium conditions, solidification occurs at a single temperature called the freezing temperature. In the case of alloys, solidification occurs over a temperature range [5], [6], [30]. Solidification begins with nucleation, followed by the growth of nuclei and a coalescence of the forming grains. This process continues with increasing fraction of solid and terminates when all of the liquid metal transforms into solid [9], [15], [32].

2.2.1 Solidification of Metals and Alloys

Nucleation can be defined as the formation of a small solid particle surrounded by a liquid phase [32], [33]. There are two types of nucleation modes experienced during solidification: homogeneous and heterogeneous nucleation.

2.2.1.1 Homogeneous Nucleation

Homogeneous nucleation occurs when spontaneous clustering of atoms forms a solid nucleus [6], [15], [32]. The atomic clustering occurs due to a change in the Gibbs free energy [5], [32]. The free energy of a system always tends to its lowest state for the given environmental and atmospheric conditions. When a metal is held in a molten state at a temperature above the freezing temperature, the liquid phase has a lower energy state than the solid phase, and thus the liquid phase is in equilibrium. Once the temperature decreases below the freezing temperature, the free energy balance shifts, with a subsequent growth of
the solid phase [5], [32], [33]. In other words, the change in the change in Gibbs free energy is related to the temperature difference between the freezing temperature and the absolute temperature.

The stability of the solid nuclei depends on their two characteristics: i) the contribution of the particle’s volumetric free energy, and ii) the contribution of the interfacial free energy, shown in Figure 2-2a. Both contributions are governed by the radius of the newly formed and growing nucleus [5], [33]. The combination of the two factors is referred to as “the total Gibbs free energy change” of the system and this must be negative or approaching negative for a process to proceed spontaneously.

![Diagram](image.png)

**Figure 2-2**: Curves representing the (a) volume and surface free energy contributions to the total Gibbs free energy for the formation of a spherical nucleus, and (b) a representation showing the critical nucleus radius for survival [5]. Adapted from *Material Science and Engineering: An Introduction, 7th edition*, p. 314, W.D. Callister. Copyright © 2007 by John Wiley & Sons Inc, New York: Reprinted with permissions from Wiley & Sons Limited.

In Figure 2-2b, a critical particle radius occurs when $\Delta G^*$ reaches the maximum positive value, and corresponds to the instance where the growing nucleus may survive and further grow to form or grain, or it may dissolve back into the melt. [5], [32], [33].

The critical radius of the nucleus is strongly influenced by the undercooling the material experiences during the initial stages of solidification [32], [33]. Undercooling is a non-equilibrium phenomenon, where the metal cools past the liquidus point without forming any
solid. The critical radius of the nucleus is inversely proportional to undercooling; a larger amount of undercooling would allow for smaller nuclei to be stable. Undercooling is, therefore, one of the driving factors for homogenous nucleation [32]. However, homogenous nucleation rarely occurs in industrial castings, since attaining an appreciable amount of undercooling is challenging. Additionally, mold surfaces, alloying elements, and impurities present in the alloy system force heterogeneous nucleation to preferentially occur. Consequently, heterogeneous nucleation is the dominant mode of solidification in practical metal casting applications [6], [15], [32].

2.2.1.1.2 Heterogeneous Nucleation

Heterogeneous nucleation requires the presence of an inoculating surface. The surface can be either a solid particle present in the melt, or it can be (for example) the wall of the mold used for the casting operation [5], [32], [33]. The wettability of the liquid metal on the inoculating surface is characterized via the wetting angle [5], [32], [33]. Figure 2-3 shows the contact or wetting angle between the nucleus and the substrate.

Ideally, the wetting angle should be as small as possible, to minimize the interfacial energy which as previously discussed, opposes the survival of nuclei [5], [32]. The magnitude of the wetting angle is governed by the lattice spacing mismatch at the metal-mold interface, or by the chemical compatibility between the liquid metal and the substrate [5], [32], [33].

Addition of inoculating particles may enhance the formation of stable nuclei and force rapid heterogeneous nucleation throughout the melt [3], [24], [25], [34]. Phase additions can also refine grains by activating new grains and slowing down the growth of already present nuclei in the melt [8], [26]. Alloying additions can also cause rapid heterogeneous nucleation of grains due to the abundance of nucleating surfaces and non-equilibrium chemical conditions [26], [35], [36].

2.2.2 Grain Refinement of Mg Alloys

Grain refinement of Mg alloys is important to enable a wider implementation of the alloys in diverse industrial applications. However, grain refinement of Mg alloys has achieved only a limited success. Some of the key challenges of grain refining Mg alloys stem from the very low density of the Mg matrix, or the presence of alloying elements which interfere with grain refinement, or the incompatibility of the grain refining particles with the Mg matrix [3], [26], [37].

The low density of Mg alloys makes a uniform distribution of inoculating particles of higher or lower density difficult, since settling or flotation of particles readily occurs [8], [34], [38]. Further, the method in which the particles are introduced into the melt is also important. If the particles are introduced as bulk powders, particle agglomeration rapidly occurs, resulting in poor inoculant dispersion. To combat this issue, master alloys are commonly used, where the master alloy is a pre-manufactured solid mixture of the refining particles suspended in a matrix. The matrix needs to be compatible with the alloy system to be grain refined.

Once the inoculating particles are dispersed homogenously in the liquid melt, the interaction with the alloying elements present in the alloy may affect the particle’s grain refining potency, since undesirable chemical reactions may occur between the inoculating particles and the alloying elements, leading to the poisoning of the grain refinement process [3], [4], [26], [30]. Predicting these reactions can be difficult, since they may only occur at high
temperatures and in very small quantities. This makes investigating the fundamental principles of grain refinement in Mg alloys difficult.

2.2.2.1 Grain refinement of Aluminum-Free Mg Alloys

The most effective grain refiner for Al-free Mg alloys is Zirconium (Zr) [24], [25], [26], [39], [40]. This has been proven extensively in the literature in many experimental studies. Zr is said to form as cores in the center of Mg grains through peritectic reaction, whereby Zr reacts with liquid Mg, and nucleates the primary Mg phase during solidification [24], [27].

2.2.2.2 Grain refinement of Aluminum-Bearing Mg Alloys

Zr is not an effective grain refiner for Mg alloys containing Al, because Zr readily forms a stable intermetallic phase Al₃Zr [35], [36], [39]. This stable intermetallic phase continually forms, exhausting all available Zr and therefore reducing the Al content of the alloy; no grain refinement is observed as a result. Other grain refiners were explored, but only limited success has been reported in the literature [24], [36], [37], [41]. The refiners examined for Al-containing Mg alloys were grouped into Titanium(Ti)-based and carbon(C)-based grain refiners. Literature on non-traditional grain refiners is also available (e.g., refinement with boron or oxide-based refiners), but these refiners never exhibited the same level of efficiency as the Ti- and/or C-based refiners [8], [35], [42]. Furthermore, other methods of grain refinement have been proposed, such as superheating the melt ~200 °C above liquidus or using an ultrasonic probe to induce nucleation during solidification, but neither of these methods were demonstrated as practical [26], [43], [44].

2.2.2.2.1 Titanium-Based Refiners

Many of the Ti-based grain refiners explored for Mg alloys were adopted from prior research on Al alloys [9], [11], [21], [45], [46]. Refinement with Ti particles, Titanium Carbide (TiC),
Titanium Boride (TiB₂), and Titanium Aluminide (TiAl₃) has been reported in the literature. These inoculants were seen to be very potent in Al alloys, but exhibited only minor effect on the grain size of Mg alloys [26].

Grain refinement of Mg alloys by Ti has been attributed to peritectic solidification reaction similar to Zr, as previously discussed (Section 2.2.2.1) [47]. Unfortunately, the solubility of Ti in Mg is low as compared to Zr (0.006 wt% Ti vs. 0.45wt% Zr) and hence the peritectic reaction of Ti alone may not be able to provide a sufficient amount of nucleating surfaces for the α-Mg phase [25], [47]. Alternatively, Ti is reported to have a high growth restricting ability of the primary phase [25], [47], [48], [49], [50]. Ti was reported to inhibit grain growth by interfering/restricting the growth of the solid phase due to the slow diffusion of Ti at the solid-liquid interface during solidification. Finally, Ti has an HCP crystal structure with comparable lattice parameters as Mg [29], which would suggest Ti could be a potent nucleant substrate, considering the lattice relation.

TiAl₃ has been used in conjunction with TiB₂ in a master alloy with a bulk composition of Al-5Ti-1B. This grain refiner formulation has been found to be highly effective in Al alloys [6], [21], [46], [51], [52] and in recent literature some suggest it is effective in Mg alloys [8], [38], [49], [53], while other literature proves otherwise [54]. It was hypothesized that TiB₂ acts as a heterogeneous nucleant, while the TiAl₃ dissolves (at temperatures >700 °C) to produce free Ti for grain growth restriction [48], [49], [55], [56]. Additionally, the TiAl₃ has also been suggested to provide further heterogeneous nucleation depending on its particle size [57]; this is likely related to the free growth model [58], [59], [60]. The free growth model suggests the nucleation potential of a particle depends on the relationship between the particle size and critical radius of the nucleus [58], [59], [60]. A more advanced model based on planar disregistry [8], [59], [60], relates the nucleation potential of a phase based on the crystallographic relationship between the nucleant and the matrix. The planar disregistry should ideally be <12% [8], [60] for good nucleation potential. The disregistry between Mg
and TiB₂ is ~5%, while Mg and TiAl₃ is ~11%, [8], [25], [57], [56]. Evaluating both disregistry and free growth, the particle size of TiAl₃ would likely need to be larger than that of TiB₂ to produce a similar nucleation potential [57], [60]. This has been observed experimentally, where refiners with larger TiAl₃ particles produced greater refinement [57], [60]. It was also stated that smaller TiAl₃ particles would most likely dissolve, which was suggested previously to beneficially induce growth restriction by providing free Ti. TiC was also explored [24], [61], [62], [63] but exact details on the effectives are not present. Other literature suggests that TiC may act as an heterogeneous nucleation site due to its low planar disregistry with Mg (only ~4%) [25], [57]. Additionally, TiC in the presence of high Al content may degrade to form the Al₄C₃ phase (temperatures >800 °C) [64]. Additionally, the Ti would likely contribute to growth restriction, although this is not discussed but based on the dissolution of TiAl₃ previously discussed. Despite the numerous research results published in the literature, a definitive description of the effect of TiC on the grain refinement in Al-bearing Mg alloys remains elusive [24], [62], [41], [65].

### 2.2.2.2 Carbon-Based Refiners

The most efficient carbon-based grain refiner reported for Al-containing Mg alloys to-date is Hexachloroethane (C₂Cl₆) powder [24], [37]; however, C₂Cl₆ produces toxic chlorinated hydrocarbon gas and thus poses severe environmental risks [8], [37]. The reported grain size reduction with Hexachloroethane reached up to ~50-70% of the base Mg alloy [37], [66], [67]. Some of the alternatives to C₂Cl₆ researched were a pure carbon powder, Carbides (e.g., SiC, TiC, Al₄C₃), MgCO₃, CO₂ gas infusion and FeCl₃ [24], [25], [36], [34], [35], [37], [68]. Refinement with carbon-based compounds is economically attractive, since graphite powder is readily available and is inexpensive. However, all of the reported studies revealed that the carbon-based inoculants and grain refiners readily agglomerate and therefore costly dispersion techniques were necessary [36], [37].
The fundamental mechanisms behind carbon inoculation proposed in the literature have not changed since their first postulation. It was suggested that when carbon or a carbon-based phase is added to Al bearing Mg alloys, the carbon reacts to produce Al₄C₃ [34], [35], [60], [62]. Based on planar disregistry, the Al₄C₃ serves as a good nucleant for the α-Mg phase [41]. In addition to forming Al₄C₃, recent literature suggests that the Al₂MgC₂ phase may also form and contribute to heterogeneous nucleation due to its crystallographic match with the α-Mg phase [26], [69], [41], [60]. However, a definitive identification of the nucleating particle was not possible, since both aluminum-carbides react with etchants and thus their identification was difficult [34], [60], [62], [70]. Unfortunately, in-situ analysis of carbon inoculation during solidification has not been reported to-date.

2.3 Hot Tearing

Hot tearing is considered one of the most detrimental casting defects for numerous Mg alloy casting processes, including sand casting, permanent mold casting, high-pressure die casting, as well as investment casting [1], [2], [6], [19], [23]. Hot tearing is a common (but complex) phenomenon that occurs during casting solidification, resulting in a permanent crack in the casting [1], [2], [3], [4], [6], [7], [9], [15], [30], [32], [33]. Hot tears are found primarily in casting areas with stress concentrations, such as 90⁰ corners or transitions between thin- and thick-casting Sections [6], [17]. If the stress concentration regions are allowed to solidify last, they are often referred to as “hot spots” and readily nucleate hot tears. Figure 2-4 shows a small hot tear in a Mg casting in a stress concentration region.
Theories aimed to predict hot tearing have focused on identifying hot tear nucleation and propagation in steels and Al alloys, but only limited success was observed with predicting hot tear behavior in Mg alloys [7], [9], [45].

2.3.1 Hot Tearing Theories

Hot tearing is often also referred to as hot cracking or hot shortness [16], [27], [45], [71]. Hot tearing occurs when a casting is physically constrained (e.g., by a metal mold) from freely contracting during volumetric shrinkage during solidification [7], [13], [16], [72], [73]. Hot tear nucleation and propagation has been exhaustively summarized by Rappaz et. al. [13], with further expansion on the topic by Gunde et. al. [16] and Stangeland et. al. [73]. Initially, grains nucleate and are surrounded by liquid. At a fraction of solid of ~0.2-0.4, the dendritic coherency point is reached and grains (or dendrites) begin to impinge on one another [9], [13], [10]. At this dendritic coherency point, the grains can still move past one another and liquid metal feeding through the growing solid dendritic structure is still relatively
easy. As solidification and solidification shrinkage continues, the tensile coherency or rigidity point is reached at a fraction of solid of ~0.6-0.8. At this instance, the dendritic structure forms a continuous solid network and is able to sustain and transmits load [10], [74], [75], [76]. After this point, effective liquid feeding through the semi-solid alloy is crucial to alleviate or prevent hot tearing. Proper casting geometry design and slow cooling may facilitate the liquid metal to compensate the casting volumetric shrinkage by directionally filling the casting from the downsprue or the pouring cup. For example, in Figure 2-5, liquid metal initially freely flows into the regions between the dendrites. Near the end of solidification (fraction of solid >0.8), the liquid metal may not be able to flow into the interdendritic channels as these can become blocked. Consequently, solidification shrinkage may not be compensated by incoming liquid, and an interdendritic porosity forms. If this porosity forms in casting regions with a stress concentration, the pores will also act as micro stress concentrations and the force developed in the casting due to shrinkage may overload the dendritic structure and nucleate a hot tear [13], [16], [73].

Figure 2-5: Developing dendritic structure showing restricted interdendritic feeding.
The above description provides a basic overview of a complex phenomenon. Several theories on the mechanisms for the nucleation and growth of hot tears were proposed in the literature [7], [8], [9], [10], [73], [74]. These include a strain-based theory, stress-based theory, thermal model, and a pressure-driven hot tear nucleation theory. Though these theories use diverse thermo-mechanical and fluids concepts, most of these theories only provide mathematical indication of where hot tears may occur in a casting or the relative severity of a hot tear, since these theories are based only on qualitative data. Quantitatively, relating the development of porosity, liquid filling, solid phase development, and the stress distribution with regards to the nucleation of hot tears remains a key challenge for researchers and metal-casters [17], [77].

### 2.3.2 Factors Influencing the Severity of Hot Tears

The main factors which influence the nucleation of hot tears include the casting geometry, liquid feeding capacity near the end of solidification, microstructure evolution, cooling rate during solidification, and the compositional variations of the alloy.

#### 2.3.2.1 Effect of Casting Geometry on Hot Tearing

The mold geometry is often the first factor to consider when dealing with the possibility of hot tearing in an industrial casting [4], [6], [15], [30], [45], [71]. In a casting with a relatively simple geometry, such as a cylindrical billet cast via direct chill method, hot tearing can occur [78], [79], [80] at the exterior of the billet as it solidifies. As solidification progresses into the interior, shrinkage porosity may begin to form in the interior of the casting if inadequate feeding is available [78], [79]. At the same time, stress and strain gradients develop and increase in magnitude through the cross-section due to the non-homogenous solidification. If the casting is not able to accommodate the stress and strain, hot tears may propagate through the cross-section, likely enabled by pores. The hot tearing mechanisms
in cylindrical billet casting are similar to the fundamental mechanisms previously discussed in section 2.3.1.

For complex 3D geometries, hot tearing is exaggerated by the stress concentrations in the geometry [15], [30], [45], [71]. A common stress concentration is a $90^\circ$ corner; similarly, casting regions where the cross-sectional areas suddenly vary also create a stress concentration [6], [7], [17], [45]. As a result, casting designers seek to reduce potential stress concentrations by making the cross-Sectional transitions smooth and gradual whenever possible. [6]. As the primary purpose of implementing Mg alloys in industrial components is to reduce the component weight, then re-designing the mold (and casting) geometry by increasing Section thickness transitions inherently adds mass to the casting. Consequently, this approach is often counter-productive towards the overall design objectives.

2.3.2.2 Effect of Liquid Feeding on Hot Tearing

Hot tearing nucleates when feeding of liquid metal is insufficient to accommodate for the solidification shrinkage experienced by the alloy after pouring of the liquid metal into the casting mold [7], [13], [73]. Sufficient liquid metal feeding throughout the entire geometry of the casting would likely result in a tear free casting [7], [9], [13], [73], [81]. However, from practical standpoint, this is a challenging task to achieve, since the temperature distribution in a casting during solidification is not uniform and enforcing directional solidification may be technologically or economically difficult.

When micro hot tears nucleate during solidification, adequate liquid metal feeding can back-fill these tears and thus enhance the integrity of the casting in a hot-tear prone region. Sufficient liquid feeding in Mg alloys to eliminate porosity is difficult as Mg castings typically solidify rapidly due to a high thermal conductivity of Mg (150 W/m²) [2]. Mg alloy castings experience high heat dissipation at mold interfaces and in thin-wall Sections, which results
in Sections of the casting becoming isolated from liquid feeding as a result of highly non-uniform temperature profile in the casting. Such non-uniformities make adequate liquid feeding through interdendritic channels at the end of solidification challenging.

2.3.2.3 Effect of Grain Size on Hot Tearing

The microstructure of the alloy is also important in determining whether a hot tear will nucleate and grow [7], [13], [17]. Fine grained microstructures have more interdendritic channels for feeding during the late stages of solidification, and thus are able to heal incipient hot tears more effectively than alloys with a coarse microstructure [23], [82]. Also, an alloy with a fine grain structure enables better stress distribution, thus reducing the effect of stress concentrations [6], [32], [83].

2.3.2.4 Effect of the Cooling Rate on Hot Tearing

The cooling rate of the alloy during solidification is one the most influential parameters used to manipulate the susceptibility of an alloy to hot tearing [7], [9], [14], [18], [19], [20], [28]. As previously stated (Section 2.1), the cooling rate represents the rate for the alloy to pass from liquidus to solidus temperatures. If a casting is able to solidify slowly (i.e. low cooling rate), the magnitude of the thermal strain is reduced, and there is also more time when liquid feeding can compensate volumetric casting contraction [14], [75]. The thermal strain induced in the casting is likely due to temperature gradients within the casting which are caused by inhomogeneous cooling rates (i.e., fast cooling and slow cooling adjacent regions of the casting) [7]. Typically, in the case of Mg alloys, the required cooling rates to eliminate hot tearing are significantly lower than for other alloy systems (e.g., Al alloy castings or steels) [6], [9], [22], [32].

The cooling rate is influenced by the pouring temperature of the alloy [18], [19], [20], [21], [28] but this effect is considered minor in comparison to the influence of the mold
temperature [18]. Melt superheating (> 150 to 200 °C) is energy intensive and may result in burning-off of alloying elements present in the alloy system. Furthermore, superheating would also cause an increased likelihood of oxide formation in the melt [18], and therefore increased likelihood of an oxide inclusion within the casting. As a result, much research has focused on manipulating the mold temperature rather than the pouring temperature of the melt.

Available literature suggests that manipulating the mold temperature is more beneficial and practical than manipulating the pouring temperature [7], [9], [12], [18], [27], [28], [71]. This practice has been shown to be consistent across multiple alloys and alloy systems. The mold temperature needed to result in a complete elimination of hot tearing is typically ~50 – 70 °C below the solidus temperature of a given alloy [9], [18]. In the AZ91D Mg alloy where the solidus is ~437 – 430 °C, this would mean a high mold preheating temperature near ~370 – 350 °C would likely be required to eliminate hot tearing. Similar to superheating the melt, this can be energy intensive, especially since the mold is often significantly cooled before casting ejection. Furthermore, such mold preheating produces a lower cooling rate which results in extensive grain growth, leading to poor mechanical performance of the final casting [22], [27], [28]. The relationship between the cooling rate and the grain growth has been extensively discussed in fundamental literature on alloy solidification [5], [6], [15], [32], [33].

Discussing the AZ91D Mg alloy specifically, several authors have proven the relationship between cooling rate and hot tearing in this alloy. Huang et. al. [18] and Bichler et. al. [84] showed that a mold temperature of 368 °C and 380 °C, respectively, was required to produce a low enough cooling rate to eliminate hot tearing in AZ91D Mg alloy, although the exact cooling rate was not reported. This mold temperature is similar to what was predicted previously. Huang et. al. [18] and Bichler et. al. [84] showed that superheating had minimal effect as compared to the mold temperature.
2.3.2.5  Effect of Alloy Composition and Additives on Hot Tearing

The composition of the alloy influences its hot tearing susceptibility via the alloy’s solidification range [3], [16], [27]. For example, increased Al content in Mg alloys has been observed to improve the hot tearing resistance and decrease the onset temperature of tear nucleation [20], [27], due to the decrease in the solidification range and increased amount of low melting temperature eutectic phases available to support liquid feeding at the end of solidification [1], [2], [19].

Mg alloys with a Zn content of ~2 – 4wt% have the largest hot tearing susceptibility [7], [17], [23], [85]. As the Zn content increases, the solidus temperature is lowered and the solidification range is increased, both of which make the alloy more susceptible to hot tearing [75], [85]. Beyond ~2 – 4wt% Zn, the amount of liquid at the eutectic composition available for feeding increased enough to refill any nucleating hot tears as they form during solidification [23], [85].

Addition of ~ 2 – 4 wt% Calcium (Ca) to Mg was observed to improve hot tearing resistance [86], due to a reduction of the freezing range, and increased formation of eutectic phases. The shorter freezing range reduces the time the material exists in the semi-solid range (i.e., time duration from the rigidity point to the end of solidification), which corresponds to the most vulnerable solidification stage for hot tear nucleation [86]. Also, it was noted that an increase in the volume of liquid with eutectic composition enhanced feeding or healing of nucleating hot tears and re-distribution of solidification stresses at the end of solidification. The increase, although not directly stated, was attributed to the presence of additional eutectic phases (e.g., Mg$_2$Ca and Al$_4$Ca$_2$) present in the alloy.

The addition of rare earth elements like Lanthanum (La), Cerium (Ce), and Neodymium (Nd) was seen to increase the hot tearing susceptibility of Mg alloys when the additions exceeded
~2wt% [74], [82], [85]. The increased susceptibility was attributed to the presence of intermetallic phases at the grain boundaries, which hindered interdendritic feeding [19].

### 2.3.2.6 Effect of Grain Refinement on Hot Tearing

There is extensive literature examining the effect of grain refinement on the hot tearing susceptibility of Al alloys [6], [11], [14], [21], [45], [52], [71], [81]. In some of the studies, grain refinement of Al alloys was achieved by the addition of Ti, B, Sr, Sc, Zr, and Nano-Particles in the form of SiC, AlN, and Al₂O₃. The most successful route for reducing hot tears in Al alloys via grain refinement, was with the addition of the well-known Al-Ti-B refiner.

Recent work completed by Nabawy et. al [21], [71] examined the effect of the Al-Ti-B refiner on hot tearing in Al alloys. The authors concluded that the refiner caused a transition from columnar to a fine grained equiaxed grain structure, which was able to accommodate solidification shrinkage via grain boundary sliding and rearrangement. Further, the refined grain size would often facilitate better feeding around the grain boundaries, thus reducing solidification shrinkage porosity (often considered a precursor to hot tearing) and ultimately reducing hot tears.

However, in the case of Mg alloys, the literature is very limited. In the last decade, merely three publications on the effect of grain refinement on hot tearing in Al-bearing Mg alloys have been published [7], [27], [53]. In the work by Elsayed et. al [53], Al-Ti-B refiners were added to AZ91E Mg alloy and the impact on hot tearing was investigated. The research focused on comparing the Al-5Ti-1B commercial refiner with a manufactured Al-3Ti-1B refiner. The hot tearing results indicate that the Al-3Ti-1B refiner significantly reduced hot tearing with a grain size of 72 μm. In other recent literature [6], [42], [54], it was found that the Al-Ti-B refiner was not effective in AZ91 Mg alloys. Other literature on the relationship between grain refinement and hot tearing in Mg alloys focused on Zr refinement in Al-free alloys [7], [27].
Thus, the precise mechanisms active during grain refinement of Al-containing Mg alloys and
the effect of grain refinement on hot tearing remains unclear. As refiner additions are often
at very low concentrations, the refining particles are difficult to locate within the casting
making their direct tracing and characterization within the alloy extremely challenging [8],
[26].

2.4 Spark Plasma Sintering (SPS)
Spark Plasma Sintering (SPS) is a powder metallurgy manufacturing process used to
consolidate (or sinter) powdered materials into bulk solid materials under controlled
temperature and pressure conditions.
Recently, spark plasma sintering has gained much interest in R&D efforts towards the
development of new materials. Unlike other sintering techniques, SPS applies electric
current and mechanical pressure during powder consolidation process to rapidly heat the
material and achieve ~99% of the theoretical density of the material. Furthermore, the
process can be completed under high vacuum or a controlled gaseous atmosphere. A
schematic of the SPS process is illustrated in Figure 2-6.
The major process parameters in SPS are the sintering temperature, sintering pressure, as
well as the heating/cooling rates, and the sintering time.
The temperature of the sintering die (and the powder within the die) is controlled via pulsed direct current [87], [88]. Two heating methods can occur depending on the electrical conductivity of the powdered material to be sintered. If the powder is electrically conductive, energy can be dissipated directly in the powder leading to an increase of the powder temperature. However, if the powder is not electrically conductive, then Joule heating and conductive heat transfer are the primary modes of heat transfer into the powdered material [89].

High mechanical loads can be applied to the powder during the sintering process. Commonly, graphite tooling is used and allows for sintering pressures of up to ~100-150 MPa [89]. Higher pressures have been applied in SPS if tungsten carbide tooling was used [88].

The SPS process can result in the successful diffusion of the powder metal matrix and any additive particles, which often results in an atomic level bond [90]. In terms of grain refiners,
this may improve the particle’s effectiveness through a newly present diffusion layer that would not be present without the SPS manufacturing process. Only a few studies are available on SPS processing of grain refiners [41].
Chapter 3: Experimental Procedure

This chapter provides a comprehensive description of the experimental procedures performed during the dissertation research. Details pertaining to the mold design, custom in-situ data acquisition system, casting procedures, grain refiner manufacturing, neutron diffraction studies and subsequent data analysis are provided.

3.1 Casting Apparatus

The casting apparatus used in this research consisted of a unique constrained rod casting mold with the capability to measure the contraction load and temperature during solidification. Two identical setups were constructed during the scope of this research to increase casting production volume.

3.1.1 Hot Tearing Mold

The steel hot tearing mold was designed by Zhen and Hort [14] and is shown in Figure 3-1. The mold consisted of a vertical downsprue and a horizontal rod oriented at 90° with respect to the downsprue. The horizontal rod Section was also designed with a slight taper to allow a low friction contraction during solidification. Extensive literature on hot tearing analysis using this mold for various alloys and casting conditions is available in the literature [14], [17], [22], [23], [27], [28], [75], [82], [91], [92]. In-depth work on the repeatability of this mold setup was published previously [14] and validated by the author (Appendix A).

At the onset of this research project, it was envisioned to use neutron diffraction to study in-situ hot tearing evolution during metal solidification. Due to the availability of the neutron source, this approach was not pursued and thus the hot tearing mold developed by Zhen and Hort [14] was selected as an alternative.
Figure 3-1: Horizontal constrained rod casting mold fitted with a load cell; (a) isometric view, (b) side cross-Sectional view, and (c) threaded rod interface region.
As the molten metal entered the mold, the pouring cup ensured a laminar flow of metal into the downsprue, and subsequently into the horizontal rod. The load evolving in the horizontal rod during solidification and ensuing contraction was transferred from the horizontal rod via a M8 threaded rod to a S-type load cell (Omega, LC101-500).

The M8 threaded rod was fabricated to allow 2.5 cm of exposed length of the rod for the liquid metal to grip it during the mold filling process. The threaded rod was used in conjunction with the coupler to allow disconnection after the casting process (threaded rods were sacrificial). As shown in Figure 3-1c, a cylindrical graphite plug was used to at the end of the horizontal rod, which filled a small gap between the threaded rod and mold, preventing liquid metal from flowing out of the mold. Furthermore, as shown in Figure 3-1c, to allow only gases to exit the mold during casting, a 1 mm slot along the entire length of the threaded rod was machined.

The mold design provided a large stress concentration in the casting at the 90° junction between the downsprue and the horizontal bar. Throughout this dissertation, this region is referred to as the "critical hot tear region". As per the design, the contraction of the horizontal rod was restricted on the left by the downsprue, and on the right by the threaded rod connected to the load cell. The connection of the load cell to the horizontal rod via the threaded rod provided in-situ data on the solidification force evolution in the horizontal bar during the bar’s solidification.

3.1.2 Data Acquisition and Calibration

The control system shown in Figure 3-2 recorded the in-situ temperature and force evolution in the casting, as well as it was used as a feedback controller to maintain the mold temperature at a desired set-point temperature.

A Data Acquisition unit (DAQ) (Omega, OMB-DAQ-56) set to a scan rate of 2 Hz, in conjunction with a 1.2 kN load cell (Omega, LC101-500) and a 0.5 mm (diam.) K-type
Thermocouple (TC) (Omega, TJC36-CASS-020E-24) were used to record the force and temperature during casting solidification. The 0.5 mm (diam.) TC located at the center of the critical hot tear region collected temperature with minimal intrusion to the natural casting solidification.

The load cell used an excitation voltage of 5 V, provided by a power source/amplifier controller that also provided analog output to the DAQ. The control system also included a mold heater (a 300W electric resistance heating tape (Omega, SWH171-020)) connected to a temperature-controlled set-point PID controller (Omega, CN4316-DC1-R2).

Calibration of the TC’s in the control system was completed by subjecting the TC to heat sources of known temperatures (e.g., boiling water at 100 °C). Also, the 1.2 kN load cell was calibrated using a 25 kN Instron load frame in the CRN laboratory at the University of British Columbia. Since the load cell operated based on the measurement of voltage differential, the load cell was calibrated so that 1 mV of induced voltage in the load cell equated to 1 N of force.
3.2 Casting Procedure

The production of AZ91D Mg alloy castings was divided into three stages. The first stage included pre-pouring procedures, which included the mold and ingot preparation. The second stage involved the casting and grain refining of the AZ91D Mg alloy, while the third stage involved the post-pouring procedures (e.g., mold disassembly and casting ejection).

3.2.1 Pre-Pouring Preparation

Prior to mold assembly, each piece of the mold was inspected and checked for any damage. As the mold was assembled, the threaded rod was attached to the coupler such that a length of 2.5 cm of threaded rod penetrated the mold cavity. After assembly of the mold as shown in Figure 3-3, the heating tape was applied.

![Figure 3-3: Hot tear mold prepared for casting.](image)

The electrical resistive heating tape was wrapped around the entire mold, covering most of the surface. Preheating of the mold took ~30 minutes and an additional 30 minutes of
holding at the set temperature to ensure the mold temperature was homogeneous. Further, the mold was covered with an insulating blanket to maintain a consistent mold heating process between each casting trial.

During the mold preparation period, an electric resistive melting furnace was preheated. Approx. 1000 grams of AZ91D Mg alloy, with a composition shown previously in Table 2-1, was melted to 740 °C in a mild steel crucible. Figure 3-4 shows the configuration of gas piping which allowed the crucible in the furnace to be covered with a constant carbon dioxide atmosphere to prevent ignition and oxide formation of the Mg melt during processing.

![Figure 3-4: Melting furnace with cover gas piping configuration sitting on the crucible.](image)

As discussed in the literature review, the pouring temperature generally has a lower impact on hot tearing and cooling rate in comparison to the mold temperature. Therefore, the
pouring temperature was fixed at 720 °C for all casting trials. This pouring temperature was sufficient to completely fill the casting cavity without any misruns.

The mold temperature was increased from 200 °C, in increments of 25 °C (i.e., casting trial at each step), until hot tearing was eliminated in the unrefined AZ91D Mg alloy. The two mold temperatures below the hot tear elimination mold temperature were then used for grain refinement trials, since these conditions were directly related to the onset of hot tearing in the AZ91D Mg alloy.

3.2.2 Pouring Process

For casting trials with the unrefined AZ91D Mg alloy, the pouring sequence was initiated when the melt temperature reached 740 °C. At this temperature, the DAQ was activated. The crucible holding the molten AZ91D Mg alloy was removed from the melting furnace, and oxides that formed on the metal surface were skimmed. The melt was allowed to cool to 720 °C pouring temperature. Throughout the entire pouring process, the molten AZ91D Mg alloy was protected with CO₂ gas to minimize melt oxidation.

The melting and pouring procedure for the grain refined AZ91D Mg alloys was similar, but with one additional step prior to making a casting. Before pouring, 0.1 wt% addition of a grain refiner was stirred into the molten AZ91D Mg alloy for 30 sec and then allowed to react in the melt for 2 minutes. The 0.1wt% addition of grain refiner was selected based on industry practice, as well as to allow comparison with published literature [53], [54], [93]. For each casting condition, three repetitions were completed for each mold temperature investigated to ensure statistical validity of the observed trends.

3.2.3 Post-Pouring Procedure

Upon casting solidification, the heating tape was disconnected, and the mold was allowed to naturally cool to 350 °C. At this temperature, the now solidified casting was disconnected...
from the load cell via the coupler and the heating tape was removed from the mold, thus allowing the casting to be ejected. Figure 3-5 shows a complete casting after being ejected from the mold. The ejection temperature was maintained across all experiments and helped prevent additional hot tear opening during thermal contraction of the casting during cooling to the room temperature.

![Figure 3-5: Completed casting after ejection from the hot tear mold.](image)

### 3.3 Grain Refiner Manufacturing

Grain refiner manufacturing was completed at the University of British Columbia’s Spark Plasma Sintering laboratory using a Thermal Technology, Model 10-3 SPS machine (Figure 3-6).

The following text describes the Spark Plasma Sintering process, as well as the powder homogenization blending prior to sintering. Finally, methods for preparation of specific grain refiner blends are outlined.
3.3.1 Powder Homogenization Process

Prior to sintering, individual powder blend constituents were weighed out and homogenized in a planetary ball mill (Fritsch, Planetary Micro Mill PULVERISETTE 7). Two 100 ml Zirconia vials were filled with 50 g each of the powdered blend. As per Fritsch operations manual, eight 20 mm (diam.) zirconia mixing balls and 25 ml of alcohol were added. The alcohol was used to eliminate agglomerations during mixing but was evaporated after the mixing process was completed. The ball milling routine consisted of three, 5 min long cycles with rotation of 100 rpm. Between each rotation cycle, a 3 min rest period was implemented to avoid overheating the blend.
3.3.2 Sintering Process

The grain refiners were sintered after evaporating the alcohol from the powder blend. The homogenously blended powders were funneled into the SPS graphite tooling. Figure 3-7 shows an example of the graphite tooling filled with the powder blend and sealed with the graphite punches.

![Graphite tooling](image)

Figure 3-7: Graphite tooling for SPS (a) filled with a grain refiner powder blend and (b) sealed with the punches.

10 grams of powder was sintered per SPS cycle. Figure 3-8 shows the sintering profile used in this research. The powder blends were sintered at 470 °C and 30 MPa, for 6 mins. The sintering program was tested with pure Al and produced a pellet of ~99% density. Additionally, the pure Al pellet was used to test the effect of the Al matrix on grain refinement.
3.3.3 Grain Refiner Formulations

Several grain refining formulations were manufactured in this research. For all refiners, the matrix consisted of pure Al powder (<45 μm particle size; Alfa Aesar, 11067). To this matrix Al powder, the following ceramic particles were added:

- Titanium Diboride (TiB₂) powder (<10 μm particle size; Sigma-Aldrich, 336289),
- Titanium Carbide (TiC) powder (<2 μm particle size; Alfa Aesar, 40178),
- Titanium Aluminide (TiAl₃) powder (<45 μm particle size; Alfa Aesar, 22895),
- Carbon (C) powder (as graphite, <20 μm particle size; Sigma-Aldrich, 282863), and
- Titanium (Ti) powder (<45 μm particle size; Alfa Aesar, 10386)

The powders used were 99.5% or greater in purity. The following is the list of each grain refiner formulation manufactured, as well as the constitutive powders used to make the grain refiner:

- Al-5Ti-1B (Al, TiB₂, TiAl₃)
- Al-15Ti-3B (Al, TiB₂, TiAl₃)
- Al-5.4Ti-0.6C (Al, TiC, TiAl₃)
• Al-16.2Ti-1.8C (Al, TiC, TiAl3)
• Al-2C (Al, Graphite)
• Al-10C (Al, Graphite)
• Al-6Ti (Al, Ti)
• Al-18Ti (Al, Ti)

For each grain refiner type (i.e., Al-Ti-B, Al-Ti-C, Al-C, and Al-Ti), two concentration levels were produced. This allowed the 0.1 wt% addition to the melt to be fixed for all experiments while still investigating the effect of increased particle concentration in the grain refiner. In the industry, a grain refiner is typically added in increasing mass addition levels to examine the effect of increased concentration of the reinforcing particles. Such approach increases the overall mass of the alloy due to the increased amount of the grain refiner matrix.

In addition to the SPS manufactured grain refiners, a commercially available refiner Al-5Ti-1B extruded refining rod was also used in this research. This commercial refiner was produced through a halide salt reaction at high temperatures in molten aluminum, and was subsequently extruded into a rod [8], [46], [94]. This refiner has been commonly used in literature and industry for the grain refinement of Al alloys [46], [93], [95], [58]. A review article by Easton et. al. [95] showed that the Al-5Ti-1B refiner added to common Al foundry alloys reduced the grain size from ~2000 μm to ~600μm at the 0.1wt% addition level. The application of the Al-5Ti-1B refiner is less common in Mg alloys [49], [53], [54]. In the work by Elsayed et al. [49] and Chen et al. [53], the grain size reduction at the 0.1wt% addition level was from ~1000 μm to ~323 μm and ~422 μm to ~125 μm, respectively. In the work by Koltygin et. al. [54] no effect was observed, even with the same addition amount as in the work of Elsayed et al. and Chen et al.
3.4 Microstructural Analysis

This Section discusses the various microstructural analysis techniques implemented for the characterization of the SPS’ed master alloys and grain refined castings.

3.4.1 Metallographic Preparation

Prior to Sectioning of the castings for microstructure analysis, the castings were photographed with a Nikon DSLR camera with a 90 mm 1:1.28 macro lens (refer to Appendix B for macro images). The critical region between the downsprue and the horizontal rod was imaged in detail to capture macro view of any evolving hot tears. The samples for grain size and hot tearing analysis were extracted from the 90° corner between the downsprue and the horizontal bar, also referred to as the critical hot tear region, as seen in Figure 3-9. The sample was extracted from the casting using a high precision water-free wet saw (Leco, VC50 Diamond Saw). This cutting method mitigated any thermal and/or mechanical stresses on the microstructure.

![Sample extraction from the critical hot tear region](image)

Figure 3-9: Sample extraction from the critical hot tear region, denoted in red; (a) top view, (b) side view.
The “T” shaped specimen in Figure 3-9b was cold mounted using a two part (2:1 ratio powder to liquid) fast curing acrylic resin (MetLab, Fast Cure Acrylic Cold Mount). The mounting process encased the sample in a resin disc that was ~30mm (diam.) and ~20 mm thick.

After curing, grinding and polishing was completed with an auto-polisher (Struers, Tegramin 30). The grinding/polishing procedure was adapted from literature for Mg alloys [96] and is summarized in Table 3-1.

A sample was ground plane with a 45 μm SiC foil. Then, it was polished with 9 μm and 3 μm diamond suspensions and finally with a 0.05 μm colloidal silica suspension. Diamond lubricant and extender (Metlab BlueLube) was used to mitigate sample heating.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Suspension</th>
<th>Grit Size (μm)</th>
<th>Cooling Fluid</th>
<th>Surface, Mover Head Speed (RPM)</th>
<th>Relative Rotation</th>
<th>Force (N)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC Foil</td>
<td>n/a</td>
<td>45</td>
<td>Distilled Water</td>
<td>250, 80</td>
<td>Counter</td>
<td>5</td>
<td>Until Plane</td>
</tr>
<tr>
<td>Struers Allergo-Largo</td>
<td>Oil Based Slurry</td>
<td>9</td>
<td>Struers Blue Lubricant</td>
<td>150, 80</td>
<td>Co</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>Struers MD-Mol</td>
<td>Oil Based Slurry</td>
<td>3</td>
<td>Struers Blue Lubricant</td>
<td>150, 80</td>
<td>Co</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Struers MD-Chem</td>
<td>Colloidal Silica</td>
<td>0.05</td>
<td>n/a</td>
<td>100, 80</td>
<td>Counter</td>
<td>15</td>
<td>1</td>
</tr>
</tbody>
</table>

3.4.2 Microscopy Techniques

In this research, Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) coupled with X-ray Energy Dispersion Spectroscopy (XEDS) were used for characterization. This Section discusses the sample preparation steps for these microscopy techniques.
3.4.2.1 Optical Microscopy

Figure 3-10 shows the Zeiss Axiovert A1m optical microscope coupled with Buehler OmniMet imaging software. The magnifications available included 100x, 200x, 1000x, and 1500x. Optical microscopy (OM) was used for grain analysis, phase distribution and hot tear evaluations.

![Figure 3-10: Zeiss Axiovert A1 microscope.](image)

The microscope image analyzer calibration was performed regularly to maintain accuracy of measurements. The calibration procedure was completed with a glass calibration slide with a laser etched micron-scale and followed the software instructions. The specific image characteristics such as brightness, white balance, and exposure were adjusted during image capture to achieve optimal images.

3.4.2.2 Scanning Electron Microscopy/ X-ray Energy Dispersion Spectroscopy

A Mira Tescan3 SEM (Figure 3-11) was used to obtain high magnification images of particles and phases in the Secondary Electron (SE) mode. The Back Scattered Electron (BSE) mode was used for atomic number (Z) contrast between phases and particles of different compositions. XEDS coupled with Aztec analysis software was used to conduct
chemical analysis of the grain refiners and as-cast AZ91D Mg alloy. The samples prepared for optical microscopy were directly used for SEM analysis, without any further treatment.

Figure 3-11: Mira3 Tescan scanning electron microscope.

3.4.2.3 Grain Size Evaluation

The grain size of an as-cast material directly influences an alloy’s strength and hardness. In the present work, the grain structure was examined after acid etching followed by microscopic quantitative evaluation.

3.4.2.3.1 Etching

Polished metallographic samples of AZ91D Mg alloy were etched with acetic glycol (formulation provided in Table 3-2).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>20</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>1</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>60</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>20</td>
</tr>
</tbody>
</table>

Immersion etching for 12 seconds was sufficient to reveal the grain boundaries and phases. After etching, the sample was submerged in a beaker with alcohol to wash-off the etchant
and arrest the etching process. After etching, the sample was cleaned with an alcohol-soaked cotton ball to remove any residue left over from the etching process.

### 3.4.2.3.2 Grain Size Measurements

A standard technique outlined in ASTM E112-13 [97] was used for grain size measurement via the Heyn linear intercept method. A test pattern for the measurements across multiple lines, in a specific array was developed, as illustrated in Figure 3-12.

![Figure 3-12: Linear intercept test pattern for average grain size measurement (not to scale).](image)

The required number of intersections counted for this method should be greater than 50. The intersection counting procedure was as follows:

- If the line intersected a junction of 3 or more grain boundaries, this was counted as 1.5.
- If the line ended on a grain boundary, this was counted as 0.5.
- If the line was parallel with a grain boundary, this was counted as 1.
- All other intersections were counted as 1.

Micrographs obtained at 100x magnification were chosen for grain size measurements. Figure 3-13 shows the five locations in the as-cast sample’s critical hot tear region where
measurements were taken. At each measurement location, three fields of view were examined.

![Image](image.png)

**Figure 3-13: Grain size measurement locations through the cross Section of the critical hot tear region.**

Locations #1 - #5 enabled microstructure and grain size evaluation across the horizontal bar's cross Section in the critical region. The average grain size results reported in this thesis do not include the measurements at locations 1 and 5 (i.e., regions at the skin region of the casting), since these locations were influenced by the rapid heat transfer at the mold surface, which has caused ultrafine grains to form.

3.4.2.4 **Microstructural Analysis**

In addition to analyzing the grain size, the microstructure was qualitatively evaluated. The AZ91D Mg alloy treated with each refiner was qualitatively compared to the unrefined AZ91D Mg alloy. The eutectic phase morphology and distribution are primarily discussed given its suggested relationship to hot tearing and feeding during the late stages of
solidification [82], [98], [7], [84]. Additionally, variations in the grain morphology and shape, along with differences in the Al-Mn and Mg$_2$Si precipitate formation were examined.

### 3.4.2.5 Qualitative Hot Tear Evaluation

Initially, exterior surface tears at the critical hot tear region were imaged before casting. It was also noted that hot tears primarily nucleated at the top and bottom of the horizontal bar. Therefore, the casting sample was Sectioned vertically from exterior to interior to analyze hot tearing. The hot tears were visible at 100x magnification under OM. The length, width, and tear characteristics were visually analyzed to provide a qualitative comparison of the hot tear severity across each unrefined and refined AZ91D Mg alloy.

### 3.4.2.6 Casting Microhardness

Figure 3-14 shows the Vickers digital microhardness tester (Buehler, Wilson VH3100 Vickers and Knoop Hardness Tester) used in this research. A minimum of 30 measurements were performed on a 3 mm by 10 mm grid through the center of the critical hot tear region. The measurement conditions involved a 0.2 kg load and a 15 sec dwell time for each measurement using a diamond-tip indenter.

![Wilson VH3100 Vickers digital microhardness tester](image)

Figure 3-14: Wilson VH3100 Vickers digital microhardness tester.
3.5 Diffraction Techniques

Several diffraction techniques were used in this research to further understand the effect of grain refinement on the alloy's microstructure. This Section discusses the setup and experimental methods for X-ray Diffraction (XRD), Electron Back Scattered Diffraction (EBSD) and Neutron Diffraction (ND) techniques.

3.5.1 X-Ray Diffraction (XRD)

XRD patterns for each SPS’ed grain refiner and the constitutive powder were obtained. Also, XRD patterns were collected for each unrefined and refined AZ91D Mg alloy casting completed with a 325 °C mold temperature.

The XRD measurements were completed at the University of British Columbia’s Vancouver Chemistry Department with a Bruker Advance diffractometer with copper (Cu) K-α target. A scan angle from 0° to 110° with a step size 0.03° and a 90 second scan per interval was used.

3.5.1.1 Sample Preparation

AZ91D Mg alloy castings (unrefined and refined conditions) were Sectioned and a small disc was cut from the horizontal rod, adjacent to the critical hot tear region, using a precision diamond saw, as marked in Figure 3-15. In the case of the SPS’ed grain refiners, a small cube ~5x5x5 mm was cut from the sintered pellets.
3.5.1.2 Data Analysis

Generated diffraction data was processed using X’pert HighScore software which referenced the Inorganic Crystal Structure Database (ISCD, FIZ-2009). The raw XRD pattern was processed (removal of background, removal of K-α signal, and peak location) using the default software settings for all samples. The peaks representing the alloy or grain refiner could then be located for identification with the crystal structure database.

3.5.2 Electron Back Scatter Diffraction (EBSD)

EBSD was used for analysis of grain distribution across the horizontal bar’s cross Section and the potential preferential orientation or crystallographic texture that may have formed during solidification. The objective was to examine a potential relationship between hot tearing and any anisotropy of mechanical properties during solidification.

3.5.2.1 Sample Preparation

For consistency, the samples used for EBSD analysis were the same disc samples analyzed under XRD. The horizontal rod portion of the casting would have most likely experienced
directional solidification given the variation of geometry from the constrained rod to the
downsprue.

The samples were prepared for EBSD following the same metallographic preparation
procedures previously explained in the “Microstructural Analysis” Section. However, a nearly
perfectly flat, scratch-free, surface was required for EBSD and thus additional polishing
steps were completed, involving one repetition of the diamond and colloidal silica polishing
steps. Finally, the sample was polished with the colloidal silica suspension for an additional
cycle.

3.5.2.2 Experimental Setup

EBSD analysis was completed on a TESCAN Mira3 field emission scanning electron
microscope (SEM) fitted with a Nordlys HKL EBSD detector. Each sample was scanned at a
tilt angle of 70° to the detector. A step size of 5.00 µm at 140x magnification was used for
crystallographic texture and grain morphology analysis.

Figure 3-16 shows the scan location on the disc sample cut from the constrained rod. The
sample was scanned from the center to skin region with 5 equal scans forming a 1 mm by 6
mm area of analysis. The overall time for all 5 scans for each sample was approximately 10
hours.

Figure 3-16: EBSD scan region on sample extracted adjacent to the critical hot tear region; (a)
Side view, (b) Top view.
3.5.2.3 Data Analysis

The scan data for all 5 scans for each sample was combined into one file using Channel 5 analysis software. The EBSD data was then filtered to remove “no solution” spots where indexing did not occur by using the indexing information around the spot to provide an approximate index of the spot. Once the EBSD file was prepared, pole figures were produced. The pole figures enabled analysis of texture based on pole distribution and the multiples of uniform distribution (MUD).

3.5.3 Neutron Diffraction (ND)

ND was applied to analyze grain refinement, *in-situ*, during solidification. Based on crystallography, analysis of solidification can be completed as individual crystals (also known as grains) nucleate and grow.

3.5.3.1 Sample Preparation

AZ91D Mg alloy samples used for ND analysis were cast to near net shape dimensions in a graphite mold with a cavity of 12 mm diameter and 50 mm in length. 30 grams of the alloy were heated to 740 °C and poured at 720 °C into the graphite mold, preheated to 400 °C. For the refined alloy, 1.0 wt% of grain refiner was mixed for 30 seconds and then held for 2 minutes before pouring into the mold. After the mold cooled to room temperature, the samples were machined to final dimensions (10.6 mm diameter by 40 mm length). An example of the final sample can be seen in Figure 3-17.
The increase weight percent addition was completed to compensate for the possibility of particles settling during the extended cooling process. Given the value and limited time of the neutron diffraction solidification analysis, an increased particle density for more reliable results is preferential to using a lower addition amount where the effect may not be detected.

The grain refiners used in the cylindrical AZ91D Mg alloy samples prepared for in-situ analysis were the Al-Ti-C and Al-C. The Al-Ti-B refiner was not used in this study as Boron is known to absorb or “block” neutron’s, which would have negatively interfered with the diffraction process. Attempts to study the effects of the Al-Ti refinement in AZ91D Mg with the in-situ solidification setup were unsuccessful due to combination of factors out of the authors’ control.

### 3.5.3.2 Experimental Setup
The in-situ solidification experiments were performed using the C2 powder diffractometer at the Canadian Neutron Beam Centre (CNBC) in Chalk River, Ontario, Canada under the supervision of Dr. Dimitry Sediako. The methods, equipment calibration and data analysis techniques were developed by Dr. Sediako and published in literature [99], [100]. Figure 3-18 shows the C2 beamline with the in-situ solidification setup installed.
A neutron beam monochromatic with a Si single crystal and a (311) reflection producing a wavelength of 2.37 Å, was used for all experiments. The angle of scattering (2θ) ranged from 30º to 110º, which captured all major diffraction peaks for the AZ91D Mg alloy. The alloy sample was loaded in an oscillating furnace under a positive pressure argon atmosphere. and

The prepared sample was placed in a sample holder within the furnace, shown in the center of Figure 3-19. An oscillating furnace was used to mitigate the effect of large grains or preferential growth, improving the quality of the diffraction data [101]. The sample holder used a graphite crucible that held the cylindrical prepared sample to be analyzed. The graphite crucible was pinned in place on the end of a long probe, which allowed the sample to be “suspended” in the beam line. The probe was connected to a lid, which sealed the furnace maintaining a positive pressure argon atmosphere. Two thermocouples were used with one providing the exact temperature of the sample and the other one being used for safety override system.
The details pertinent to the solidification path imposed during the *in-situ* solidification experiments are provided in Table 3.3 each temperature was held for one hour to ensure statistically valid neutron counts. Before and after each ND experiment, a scan was also completed at room temperature to ensure that the sample did not chemically change during the experimental run.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unrefined/Refined Alloy</td>
<td>40 (0.25 hrs only), 630 (0.08 hrs only), 593, 585, 575, 565, 555, 545, 535, 525, 515, 505, 495, 485, 475, 465, 455, 450, 445, 440, 435, 430, 425, 420, 405, 300 (0.5 hrs only), 40 (0.25 hrs only)</td>
<td>26</td>
</tr>
</tbody>
</table>

### 3.5.3.3 Data Analysis

The *in-situ* solidification data analysis procedure implemented in this research was developed by Dr. Dimitry Sediako and has been referenced in multiple publications [99], [100], [101], [102], [103], [104], [105], [106].

The evolution of the fraction of solid (FS) during the cooling of the sample was calculated based on the change in the integrated intensity (i.e. area) as a function of temperature of the
{10-10}, {0002} and {10-11} reflections corresponding to the hexagonal close packed (hcp) α-Mg phase (pattern indexed with ICSD, FIZ-2009). As the solid formed from the liquid phase, the intensity of the peaks increased, corresponding to an increasing fraction of crystalline solid phase. The area of each α-Mg reflection was measured as a function of temperature and normalized relative to the area of the corresponding peak measured on the fully solidified sample. A correction factor based on the Debye-Waller (DW) effect, was applied in an iterative fashion [101], [29], [106]. The DW or temperature factor describes the decrease of peak intensities with increased temperature [29]. As temperature increases, thermal motion of atoms within the lattice increases which causes some neutrons to diffract as background instead following the specific 2θ for a particular crystallographic plane [29]. These calculations were completed for each of the {10-10}, {0002} and {10-11} α-Mg diffraction peaks and the average of their normalized and DW-corrected areas was used to calculate the overall FS values as a function of temperature. The evolution of secondary phases was calculated in a similar manner. Further information on this technique is provided in Appendix C.

Phase development (in wt%) during solidification was also determined. Diffraction analysis software, MAUD (Materials analysis using diffraction), uses the Rietveld refinement technique to quantify phases in diffraction patterns. The methods used were as instructed by the software and minimal user input was needed. Using the final (room temperature) diffraction pattern, the weight percent of the α-Mg and β-Mg₁₇Al₁₂ present in the alloy could be determined. With the weight percent found of each phase, relative fraction of solid curves for both α-Mg and β-Mg₁₇Al₁₂ phases could be adjusted accordingly to show fraction of solid curves in terms of weight percent of phases present in the alloy. Further information on the application of the Rietveld refinement technique is given in Appendix C.
3.6 Hot Tearing Mold Data Analysis

This Section discusses the analysis of the in-situ data collected during casting solidification using the load cell and thermocouples placed in the casting.

3.6.1 In-situ Temperature Data

In-situ temperature data was collected during the entire solidification process. From temperature data, the cooling rate (dT/dt) could be determined following Equation 3-1 using the non-equilibrium liquidus (T_L) and solidus temperatures (T_S) of the alloy (Section 2.1.1, Appendix E) and the local solidification time (Time_L-S) from T_L to T_S.

\[
\frac{T_L - T_S}{\text{Time}_{L-S}} = \frac{dT}{dt} (\degree C/s)
\]

Equation 3-1

Throughout this thesis, castings conditions are labeled with respect to the mold temperature used to produce the casting. For castings produced at 350 °C mold temperature, the cooling rate was ~1 C/s. For castings completed at 325 °C mold temperature, the corresponding cooling rates varied from 1.5 to 2.5 °C/s, while for castings completed at 300 °C mold temperature, the corresponding cooling rates varied from 3.0 to 4.0 °C/s.

Several mathematical models exist to calculate the fraction of solid based on the instantaneous temperature data. In the present work, the fraction of solid was calculated using Equation 3-2, where T is the instantaneous alloy temperature. This model was developed by Tacke et. al. [107], and takes into consideration the assumes relatively high cooling rates experienced in solidification of industrial-scale castings, which in turn influences the concentration of solute at the solid-liquid interface. The model also takes into account solute rejection into the liquid, which modifies the local solidus and liquidus temperatures.
\[ f_s = \frac{T_L - T + \frac{2}{\pi} (T_S - T_L) \left\{ 1 - \cos \left[ \frac{\pi (T - T_L)}{2(T_S - T_L)} \right] \right\}}{(T_L - T_S) \left[ 1 - \frac{2}{\pi} \right]} \]

Equation 3-2

This fraction of solid equation was originally developed for steel casting, but over the years has found relevance in Mg alloys [9]. Additionally, the model has correlated well with the results of the fraction of solid profile developed via neutron diffraction for the unrefined AZ91D Mg alloy present in this research (Appendix C).

### 3.6.2 In-situ Force Data

In-situ force data was collected during the entire solidification process. From the force data and the local solidification time from the temperature data, force relaxations or drops related to hot tearing could be identified. Additionally, the force curves had a characteristic change in slope, labelled as the “inflection” in the force curve. Also, the force at the end of solidification, based on the local solidification time, was identified. As well, the solidification time after the inflection to complete solid was calculated. Finally, the force evolution was compared to the temperature-based fraction of solid to provide insight on the available solid when force evolved. Further information on the repeatability of the hot tearing data is provided in Appendix A.
Chapter 4: Results and Discussion

In this chapter, a comprehensive discussion of the research findings is presented. The effect of the various grain refiners on the microstructure of the AZ91D Mg alloy is discussed based on qualitative and quantitative data, followed by the analysis of the impact of the grain refiners on the solidification process and the alloy’s hot tearing behavior.

4.1 Characterization of Spark Plasma Sintered Grain Refiners

A representative image of an SPS’ed grain refiner pellet is provided in Figure 4-1. The general appearance of the grain refiners was identical to a pellet made of pure Al. No visible macro observations due to the various additives blended with the Al matrix powder were recorded.

![Figure 4-1: As-sintered 20 mm diameter grain refiner pellet.](image)

The density of each SPS’ed grain refiner was measured using the Archimedes principle. As Table 4-1 shows, the average density of the grain refiners ranged from ~80-90% of the theoretical density for each blend.
### Table 4-1: Density of SPS’ed grain refiners.

<table>
<thead>
<tr>
<th>Grain Refiners</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Al-5Ti-1B</td>
<td>90</td>
</tr>
<tr>
<td>Al-5Ti-1B</td>
<td>91</td>
</tr>
<tr>
<td>Al-15Ti-3B</td>
<td>80</td>
</tr>
<tr>
<td>Al-5.4Ti-0.6C</td>
<td>91</td>
</tr>
<tr>
<td>Al-16.2Ti-1.8C</td>
<td>83</td>
</tr>
<tr>
<td>Al-2C</td>
<td>97</td>
</tr>
<tr>
<td>Al-10C</td>
<td>94</td>
</tr>
<tr>
<td>Al-6Ti</td>
<td>93</td>
</tr>
<tr>
<td>Al-18Ti</td>
<td>88</td>
</tr>
</tbody>
</table>

The Al-5Ti-1B and Al-5.4Ti-0.6C refiner’s average density was ~90% of the theoretical density of the blends. As the concentration of the particles in the grain refiner increased, the density of the SPS’ed pellet decreased to ~80%. Since the sintering conditions were maintained constant for the manufacture of all the grain refiners, it is likely that the powder consolidation and sintering was influenced by the concentration of the additive particles. Such lowering of sinterability could be the result of increased concentration of electrically non-conductive phase, which would then lower the temperature of the Al powder matrix. As a result, pores and voids developed at the grain boundary triple points and contributed to a reduction of the SPS’ed density, which was further observed during microstructure analysis of the SPS’ed grain refiners, as discussed in the following Sections.

#### 4.1.1 SPS’ed Al-Ti-B Grain Refiner

Figures 4-2, 4-3, and 4-4 show the SEM micrographs of the SPS’ed Al-5Ti-1B and Al-15Ti-3B grain refiners, along with the commercially available Al-5Ti-1B refiner. On a macro scale, the distribution of particles appeared homogeneous, suggesting that the powder blending process prior to SPS processing was adequate on the macro scale.
As discussed in Section 4.1 earlier, in the case of the Al-15Ti-3B grain refiner, large pores were observed throughout the microstructure. The pores likely originated from incomplete fusion of grain-boundary triple points or the result of particle fall-out during metallographic preparation. However, comparing the scale of the pores and the size of the particles in the raw powder blends, it is likely that the porosity was predominantly the result of incomplete sintering.

Figure 4-2: SEM micrograph of the Al-5Ti-1B grain refiner at (a) 100x, and (b) 1000x.
Figure 4-3: SEM micrograph of the Al-15Ti-3B grain refiner at (a) 100x, and (b) 1000x.

Figure 4-4: SEM micrograph of the commercial Al-5Ti-1B grain refiner at (a) 100x, and (b) 1000x.

Figure 4-2 and Figure 4-4 show that the SPS and commercial Al-5Ti-1B refiners contained large white particles (avg. size 40-45 μm), which were identified by SEM-XEDS as the TiAl₃.
phase. In the case of the SPS Al-5Ti-1B grain refiner, the distribution of these TiAl₃ particles appeared more uniform throughout the material than in the case of the commercially available grain refiner.

The grain refiners also contained fine gray-white particles, which were identified by SEM-XEDS as the TiB₂ phase. In the SPS Al-5Ti-1B refiner, fine (<10μm) TiB₂ particles were dispersed throughout the microstructure, while in the commercial Al-5Ti-1B refiner the ultrafine TiB₂ (~2-3 μm) particles were seen to agglomerate into bands, as seen in Figure 4-4b. Agglomeration of the TiB₂ particles would decrease their efficiency to act as heterogenous nucleants [48], [49], [53]. Table 4-2 shows the results of the particle-to-particle distribution analysis based on the TiAl₃ particles in both SPS’ed and commercial refiners. The results are in agreement with the observations previously made based on Figure 4-2 and 4-4, as the standard deviation of the particle-to-particle distance shows to be much higher in the commercial refiner. Additionally, the range of the particle-to-particle distance is increased in the SPS’ed refiner was tighter, suggesting improve homogeneity of the particle distribution.

<table>
<thead>
<tr>
<th>Refiner</th>
<th>Ave. Particle-to-Particle Distance (μm)</th>
<th>Standard Deviation of Particle-to-Particle Distance (μm)</th>
<th>Range of Particle-to-Particle Distance (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS’ed Al-5Ti-1B</td>
<td>84.81</td>
<td>28.9</td>
<td>38.3 – 146.5</td>
</tr>
<tr>
<td>Commercial Al-5Ti-1B</td>
<td>93.87</td>
<td>84.3</td>
<td>13.3 – 311.04</td>
</tr>
</tbody>
</table>

As the commercial refiner was produced through a halide salt reaction followed by extrusion, dispersion of the refining particles was likely challenging, thus leading to their agglomeration. The halide salt process would have also likely resulted in the formation of a gaseous phase, which may have remained entrapped in the grain refiner. The entrapment was observed as bubble-like micro voids dispersed throughout the microstructure.
Chemical composition analysis of the SPS and commercial Al-5Ti-1B refiners with XEDS using 10 view fields per refiner at 500x magnification was completed. The analysis showed the average Ti and B concentrations in the commercial refiner was only ~Al-4.1Ti-0.4B while SPS refiner had composition of ~Al-5.3Ti-0.93B. As the SPS refiner was produced with exact proportions of constitutive powders, its composition could be accurately controlled. In contrast, the commercial refiner did not have the expected concentration of constitutive elements, which likely impacted the effectiveness of this refiner during metal casting operations.

A detailed analysis of the additives in the grain refiners was carried out with SEM-XEDS linescan analysis. This analysis focused on examining the solute gradients at the interface between the additive particles and the Al matrix. Figure 4-5 and Figure 4-6 show XEDS linescans over the TiAl₃ and TiB₂ particles in the SPS prepared Al-5Ti-1B and Al-15Ti-3B refiners, respectively. Figure 4-7 and Figure 4-8a show a XEDS map and an XEDS linescan of the TiAl₃ particles in the commercial refiner. Figure 4-8b shows a linescan of the TiAl₃ particle in the commercial Al-5Ti-1B refiner.
Figure 4-5: XEDS linescan across (a) TiAl₃ and (b) TiB₂ particles in the Al-5Ti-1B grain refiner; Al denoted by red line, Ti denoted by orange line, B denoted by green line.

Figure 4-6: XEDS linescans across (a) TiAl₃ and (b) TiB₂ particles in the Al-15Ti-3B grain refiner; Al denoted by red line, Ti denoted by orange line, B denoted by green line.
Figure 4-7: XEDS map of commercial Al-5Ti-1B grain refiner showing the distribution of Ti and Al elements.

Figure 4-8: XEDS linescans across two (a), (b) TiAl₃ particles in the commercial Al-5Ti-1B grain refiner; Al denoted by red line, Ti denoted by orange line.
The results of the XEDS linescan analysis in Figure 4-5 and Figure 4-6 show that the particle boundaries in the SPS processed grain refiners, the Al content decreased gradually on either side of the particle. In contrast, Figure 4-8 shows that in the commercially fabricated Al-5Ti-1B refiner, the Al solute concentration at the particle boundary decreased rapidly. This comparison suggests that during SPS processing, the electric discharge between the Al powder matrix powder and the additive particles (i.e., TiAl$_3$ and TiB$_2$) enabled formed an intermediate boundary layer at the particle interface. Consequently, the SPS process facilitated a form of pre-wetting of the reinforcing particles, which would significantly enhance their wettability by liquid Mg upon addition of the grain refiner into the liquid AZ91D Mg alloy [64], [108], [109]. The combined effect of enhanced wetting and a more uniform distribution of the TiB$_2$ and TiAl$_3$ particles throughout the grain refiner likely contributed to the enhanced heterogenous nucleation of the α-Mg phase during solidification and the resulting decrease in the grain size (as discussed in Section 4.2.1).

### 4.1.2 SPS’ed Al-Ti-C Grain Refiner

Figure 4-9 and 4-10 show the general microstructure of the SPS’ed Al-Ti-C grain refiners. As the concentration of the additive particles increased, the particles preferentially segregated to the interparticle regions. The Al-5.4Ti-0.6C refiner showed a good particle distribution throughout the SPS’ed pellet with only rare clustering of particles. Conversely, the Al-16.2Ti-1.8C refiner exhibited formation of particle clusters. Also, with increasing additive concentration, the amount of porosity increased and reached ~17% in the Al-16.2Ti-1.8C refiner. Interestingly, however, the porosity was predominantly in the regions rich in TiAl$_3$. 
Figure 4-9: SEM micrograph of the Al-5.4Ti-0.6C grain refiner at (a) 100x, and (b) 1000x.

Figure 4-10: SEM micrograph of the Al-16.2Ti-1.8C grain refiner at (a) 100x, and (b) 1000x.

The large grey particles in both Al-Ti-C refines were the TiAl$_3$ particles (avg. size ~40 μm).

The bright white particles in the BSE micrographs were the ultrafine TiC (< 2 μm) particles.
and were dispersed in the dark grey Al matrix or were seen to decorate the TiAl₃ particles; the latter was mostly present in the Al-16.2Ti-1.8C refiner.

Figure 4-11: XEDS map and linescan analysis; (a) map of Al-5.4Ti-0.6C, and (b) Al-16.2Ti-1.8C refiners, and linescan of (c) a TiAl₃ particle in the Al-5.4Ti-0.6C refiner; Al denoted by red line, Ti denoted by orange line, C denoted by yellow line.
Figure 4-11a and 4-11b show the XEDS maps of both Al-Ti-C grain refiners, showing the TiC and TiAl\(_3\) interaction in the refiner. In Figure 4-11a, the particle with spectrum 7 was identified as the TiAl\(_3\) and spectrum 8 and 10 were identified as the TiC particles. Figure 4-11c shows a TiAl\(_3\) particle in the Al-5.4Ti-0.6C refiner, where a similar intermediate layer boundary was observed, similar to the intermediate layer in the Al-Ti-B refiners previously discussed (Section 4.1.1).

### 4.1.3 SPS’ed Al-C Grain Refiner

Figures 4-12 and 4-13 show the SEM micrographs of the Al-2C and Al-10C grain refiners. Additionally, Figure 4-14 shows an XEDS map of the Al-10C refiner.

![Figure 4-12](image1.png)

(a) Figure 4-12: SEM micrograph of the Al-2C grain refiner at (a) 100x, and (b) 1000x.
The SEM micrographs show an extended porosity networks throughout both Al-C grain refiners. The porosity voids were frequently laced with carbon powder, as seen in Figures 4-12 and 4-13.

Despite the presence of what appeared as voids, the Archimedes density measurements revealed that the Al-2C and Al-10C refiners reached ~97% and 94%, respectively. This result is likely a consequence of the similarity in densities between aluminum (2.70 g/cm$^3$) and carbon (2.26 g/cm$^3$). The visible porosity that was observed on the polished surface was likely the result of the carbon powder being removed during metallographic preparation. In areas where carbon powder was retained, XEDS map confirmed its presence (Figure 4-14b).
The XEDS analysis of the Al-C grain refiners was impeded by the technique's inability to accurately map the carbon distribution. In addition, the variation in the topography (i.e., depth) in the pore region further hindered accurate quantitative analysis. However, the analysis revealed the presence of small particles of carbon within the Al matrix (Figure 4-14b). In these regions, the weight percent of C and Al in the particles was ~78% and ~22%, respectively. According to the Al-C phase diagram and literature [62], this weight percent combination is consistent with the Al$_4$C$_3$ phase. Further investigation via linescan was completed as seen in Figure 4-15.
The linescan in Figure 4-15 reveals a gradual variation of Al and C concentration at the particle boundaries, suggesting an intermediate layer at the particle boundary form, possibly forming the $\text{Al}_4\text{C}_3$ intermetallic phase at the particle interface. Literature suggests that these $\text{Al}_4\text{C}_3$ may be an effective nucleating substrate for Mg alloys when carbon-based refiners were used [34], [35], [60], [62].

4.1.4 SPS'ed Al-Ti Grain Refiner

Figures 4-16 and 4-17 show SEM micrographs of the Al-Ti grain refiners. In the BSE mode, the Ti particles show as bright phase and the Al matrix was the dark grey phase. Also, some SiC particles from the grinding step of the sample preparation were observed to be embedded in this grain refiner sample, despite re-polishing attempts.
The Al-6Ti grain refiner showed minimal agglomeration of the Ti particles, while the Al-18Ti refiner shows formation of Ti-particle clusters at the grain boundaries. Interestingly, both grain refiners produced similar grain refining effect on the AZ91D Mg alloy (discussed in Section 4.2), suggesting that the particle agglomeration in the SPS’ed grain refiner did not impact the refining efficiency.

Figure 4-16: SEM micrograph of the Al-6Ti grain refiner at (a) 100x, and (b) 1000x.
Figure 4-17: SEM micrograph of the Al-18Ti grain refiner at (a) 100x, and (b) 1000x.

Figures 4-18 and 4-19 show the XEDS maps and linescans, respectively, of the Ti particles in the SPS’ed grain refiner. As was also observed in the Al-Ti-B grain refiners (Section 4.1.1), the results suggest that during SPS processing, Ti readily formed an intermediate layer with Al during sintering. This was likely due to the optimal conditions for the Al and Ti to react and produce the intermetallic phase TiAl₃, based on the Al-Ti phase diagram [110]. Formation of the intermetallic phase was also enabled by Al and Ti having a similar atomic radius of ~0.1431 and ~0.1445 nm, respectively [5].
From the XEDS map and linescans, it was observed that the Al matrix has reacted and formed an intermediate layer around the Ti particles. The Al layer could be a major factor for the effectiveness in grain refining the AZ91D Mg alloy. As previously discussed in Section 4.1.1, pre-wetting of the nucleant particles would likely enhance their refining effectiveness.
Based on crystallographic similarities of Ti and Mg discussed in Section 2.2.2.2.1, pre-wetting of the Ti particle would likely enhance heterogenous nucleation of primary Mg during treatment of the AZ91D Mg alloy. Also, the Al diffused into the particle boundary may have also formed TiAl3 phase, which has been identified in literature as a possible heterogenous nucleant for Mg alloys [25], [57], [56].

### 4.1.5 X-ray Diffraction of Grain Refiners

XRD analysis of the grain refiners was carried out to examine the crystallographic phases present in the SPS’ed grain refiners. Also, it was of interest to detect any new phases forming as a result of SPS processing. Figure 4-20 shows the XRD spectra for each low concentration grain refiner including the commercial refiner, while Figure 4-21 shows the XRD spectra for the high concentration grain refiners. As expected, Al was present in each refiner represented as the 4 most intense peaks, repeated in each pattern.
Figure 4-20: XRD patterns of the low concentration grain refiners.
Figure 4-21: XRD patterns of the high concentration grain refiners.

Figure 4-20 shows that the refining particles’ concentration in the commercial Al-5Ti-1B refiner was much lower than the SPS’ed Al-5Ti-1B refiner even though similar particle concentrations should be present. This suggests the commercial refiner may have lower particle concentrations than disclosed as discussed previously in Section 4.1.1.

In the case of the Al-2C refiner, Figure 4-20 suggests that the Al peaks were easily identified, while only one peak for C, at ~26°, was detected. Given the low concentration of C in the Al-2C refiner, this result was expected since the normalized peak intensity is typically proportional to the weight fraction of the element. For both grain refiners, however, the XRD technique was not able to detect the presence of the Al₄C₃ particles, likely due to their volume fraction falling below the minimum detectability limit of the XRD system.

In the case of the Al-6Ti refiner, Figure 4-20 revealed isolated peaks corresponding to Ti, where the high intensity peaks for Ti coincided with Al. Indexing via the ICSD database
confirmed a match with the TiAl$_3$ phase. This result was further supported by comparing the TiAl$_3$ peak positions in the Al-6Ti refiner to the TiAl$_3$ peak positions in the Al-5Ti-1B and Al-5.4Ti-0.6C patterns, where the TiAl$_3$ phase was added as a constitutive ingredient into the grain refiner. Therefore, the XRD analysis suggests that SPS may have facilitated Ti reaction with the Al matrix to form TiAl$_3$. As shown in Section 4.1.4, this may be the phase of the intermediate layer.

Figure 4-21 shows similar patterns to Figure 4-20 for the respective refiners, but with increased peak intensity for the refining elements when their concentration was increased.

4.2 Grain Refinement

This section summarizes the effect of the various grain refiners on the as-cast microstructure of the AZ91D Mg alloy. The discussion includes analysis of the grain size, trends in microhardness due to refinement, and the microstructure and phase distribution of the unrefined and refined AZ91D Mg alloy.

4.2.1 Grain Size Results

Figure 4-22 shows the average grain size for each refined casting at both mold temperatures analyzed. The standard deviation of each measurement is denoted by the errors bar. The results show each SPS prepared grain refiner resulted in a significant grain size reduction of the AZ91D Mg alloy. Also, the SPS prepared grain refiners exhibited a significant reduction in the standard deviation of grain size, suggesting an improvement in the grain size homogeneity. Interestingly, the grain size results suggest that when the SPS prepared grain refiners were added, the grain size was independent of the casting mold temperature (i.e., cooling rate), suggesting that the heterogeneous nucleation potency of the grain refiners exceeded the effect of the cooling rate on the alloy grain size.
Comparing the mean values in Figure 4-22, the Al-Ti grain refiners produced the highest reduction in the as-cast grain size. At both mold temperatures and refinement concentrations, the average grain size reduced by ~79%. Although, accounting for the error the results suggest that most of the SPS‘ed refined alloys were equally effective.

The SPS fabricated Al-5Ti-1B grain refiner was seen to be effective at reducing the grain size, with an average grain size reduction of ~72-75%. In contrast, the AZ91D Mg alloy refined with the commercial Al-5Ti-1B, cast at 325 °C mold temperature, was only able to achieve a grain size reduction of ~56%. Furthermore, the standard deviation was significantly reduced in the SPS Al-5Ti-1B refined alloy. Based on these results, the Al-5Ti-1B refiner produced via SPS has outperformed the commercial Al-5Ti-1B refiner.
Figure 4-22 also reveals that for AZ91D Mg alloy treated with an equivalent weight percent addition of a SPS’ed pellet containing only the Al matrix, the grain size was only reduced by \(\sim 16\%\). However, the overlapping standard deviation for this treatment in comparison to the unrefined AZ91D Mg alloy grain size prevented a statistically significant conclusion that pure Al was capable of reducing the grain size. This result is consistent with the conclusions of Elsayed [8] where an Al-Ti-B grain refiner and pure Al were used to treat AZ91E Mg alloy. In their work, the pure Al was also reported to have a negligible effect on the grain size.

4.2.1.1 Grain Size Variation in the Horizontal Bar

The grain size was measured at five locations of the horizontal bar’s cross section to evaluate the grain size homogeneity in the critical casting region. Figure 4-23 shows the variation of grain size for the various mold temperatures with unrefined AZ91D Mg alloy. The skin regions had fine grains (due to the high heat transfer at the metal mold interface), while the grains at the center of the horizontal bar were significantly larger (possibly due to a combination of lower cooling rate facilitating grain growth and also the absence of heterogenous nucleation sites in the center region). Similar grain size variation results were observed for both mold temperatures. Interestingly, the grain size at locations 4 and 5, which corresponded to the bottom region of the horizontal bar, exhibited larger grains than the counterpart top regions (locations 1 and 2). This difference was likely the result of inhomogeneous cooling resulting from a more superheated metal entering the bottom section of the casting mold, in comparison to the relatively cooler metal present in the upper sections of the mold [34].
Figure 4-23: Grain size variation through the critical hot tear region for the unrefined AZ91D Mg alloy.

Figures 4-24 to 4-27 show the variation of grain size for each of the SPS grain refined AZ91D castings. Overall, each refiner addition produced a significant reduction in the grain size throughout the entire cross Section. Further, at both mold temperatures, the refined castings had a relatively consistent grain size. This indicates that each refiner induced heterogeneous nucleation throughout the critical hot tear region, which became the dominant mechanism for grain size reduction rather than the cooling rate effect at the metal-mold interface.
Figure 4-24: Grain size variation through the critical hot tear region for AZ91D Mg alloy refined with Al-Ti-B, cast at (a) 325 °C, (b) 300 °C mold temperature.

Figure 4-25: Grain size variation through the critical hot tear region for AZ91D Mg alloy refined with Al-Ti-C, cast at (a) 325 °C, (b) 300 °C mold temperature.
Figure 4-26: Grain size variation through the critical hot tear region for AZ91D Mg alloy refined with Al-C, cast at (a) 325 °C, (b) 300 °C mold temperature.

Figure 4-27: Grain size variation through the critical hot tear region for AZ91D Mg alloy refined with Al-Ti, cast at (a) 325 °C, (b) 300 °C mold temperature.

In the case of the SPS manufactured refiners, the Al-Ti refiners produced the finest grains while the Al-Ti-C refiners yielded the largest grains. However, in terms of grain size variation through the critical regions, each refiner was effective at producing a more homogenous grain size compared to the unrefined AZ91D Mg alloy. Literature suggests that a homogenous grain size is correlated to isotropy of the mechanical properties at room temperature [63], [111]. Further, these results could be extended to suggest isotropy of the
dendritic structure during casting solidification (refer to Appendix D for dendritic structure within grains of as-cast AZ91D). This would likely result in homogeneous stresses in the casting during solidification and possibly reduced hot tearing susceptibility of the alloy [6], [73], as will be further discussed in Section 4.4.

4.2.2 Microhardness Results

Figure 4-28 shows the results of Vickers micro hardness testing of each casting. The hardness values for the unrefined AZ91D Mg alloy castings were consistent with literature [42], [112], [113]. The hardness of the unrefined AZ91D Mg alloy, cast at 325 °C and 300 °C mold temperature, was ~59 HV and ~60 HV, respectively. The difference in hardness between the mold temperatures was statistically insignificant, given the measurement variation shown by the error bars in Figure 4-28.
Figure 4-28: Average Vickers hardness for unrefined and refined AZ91D Mg alloy.

Since the pure Al and commercial Al-5Ti-1B grain refiners had a negligible effect on the grain size, their impact on the Vickers hardness was also negligible with respect to the unrefined alloy.

The AZ91D Mg alloy treated with the Al-2C and Al-10C refiners exhibited the highest Vickers hardness, regardless of the mold temperature. In relative terms, the AZ91D Mg alloy castings treated with the Al-Ti-C grain refiners were the softest, despite being ~15 HRV units above the untreated AZ91D Mg alloy.

The hardness of an as-cast alloy could be affected by many factors such as the grain boundary density, a harder primary phase, and the presence of secondary phases resisting plastic deformation. In many of the AZ91D Mg alloys refined with SPS fabricated refiners,
the grain size was significantly reduced, thus increasing the grain boundary density. The increased grain boundary density would subsequently enhance resistance to plastic deformation. Additionally, the hard β-phase was more uniformly distributed throughout the microstructure in the SPS grain refined alloys in comparison to the unrefined AZ91D Mg alloy castings, thereby contributing to a more effective precipitation hardening.

Consequently, Figure 4-29 suggests a strong correlation between the hardness and the grain size for the SPS refined castings. According to the Hall-Petch relationship for hardness (Equation 4-1), the hardness should increase inversely to the grain size [114], [115], [116], [117]. Equation 4-1 shows the relationship where $H_o$ and $K_H$ are constants and $H$ is the microhardness and $d$ is the average grain diameter.

$$H = H_o + K_Hd^{-\frac{1}{2}}$$

Equation 4-1

The grain size-hardness proportionality followed a linear fit with $R^2 \approx 0.87$.

Al-C refined castings showed the highest hardness without the lowest grain size (i.e., lower grain boundary density). This could possibly be attributed to the Al-C refiners producing a harder α-Mg phase during solidification or a bigger contribution of the hard secondary phases. [118], [119].
4.2.3 Microstructure of Unrefined AZ91D Mg Alloy

Figures 4-30 to 4-32 show the general microstructure of the unrefined as-cast AZ91D Mg alloy. The general microstructure consisted of the α-Mg solid solution and the eutectic β-phase (i.e., Mg₁₇Al₁₂) non-uniformly distributed throughout the alloy. Large, isolated pockets of eutectic β-phase were observed at the grain triple-point junctions. Also, islands of eutectic β-phase were present inside the grains which could be due to eutectic liquid trapped within intergranular regions during solidification. Furthermore, the Al-Mn precipitates in the unrefined castings were visible. The Mg₂Si precipitates were fine particles ~1 μm in diameter not visible at the magnification levels of Figure 4-30. Also, interdendritic solidification shrinkage porosity was observed throughout the microstructure.
Figure 4-30: Microstructure of unrefined AZ91D Mg alloy cast at 350 °C mold temperature.

Figure 4-31: Microstructure of unrefined AZ91D Mg alloy cast at 325 °C mold temperature.

Figure 4-32: Microstructure of unrefined AZ91D Mg alloy cast at 300 °C mold temperature.
The grain size in the unrefined castings at the 350 °C, 325 °C and 300 °C mold temperatures was ~305 μm, ~275 μm, and ~250 μm, respectively, with a relatively large standard deviation of ~80 μm for each mold temperature. The grain size of the unrefined AZ91D Mg alloy decreased with decreasing mold temperature due to the alloy’s known grain size dependency on the cooling rate [83]. This phenomenon has been reported in the literature, as previously discussed in Section 2.3.2.4.

4.2.3.1 Eutectic Phase

The eutectic phase during non-equilibrium cooling of the AZ91D Mg alloy can manifest in several ways; i) lamellar structure, ii) partially divorced, or iii) fully divorced eutectic structure. The lamellar structure is commonly observed in sand- and permanent-mold cast AZ91 series alloys, as was also seen in Figure 4-33.

A partially divorced eutectic phase may form when islands of the eutectic α-Mg coexist within the β-phase [98]. In Figure 4-34, partially divorced eutectic structure was observed at the grain boundaries. Finally, a fully divorced eutectic (not observed in the unrefined alloy) is similar to the partially divorced eutectic structure, but the islands of α-Mg are not present,
making the eutectic a homogenous phase. The advantage of retaining the homogenous eutectic phase would be improved feeding of liquid via the eutectic phase and interdendritic channels [84] near the end of the casting’s solidification (refer to Appendix D for dendritic structure within grains of as-cast AZ91D). Such feeding would further influence formation of casting defects, such as porosity or hot tears.

Figure 4-34: Eutectic near the surface of AZ91D Mg alloy, cast at 325 °C mold temperature.

4.2.4 Microstructure of Grain Refined AZ91D Mg Alloy

The general microstructure of the AZ91D Mg alloy castings refined with the Al-Ti-B, Al-Ti-C, Al-C and Al-Ti grain refiners was examined in detail. For each grain refiner, the characteristics of the grain structure, eutectics and the second phases were discussed in relation to the unrefined AZ91D Mg alloy. Also, the microstructure of the AZ91D Mg alloy refined with the commercial Al-Ti-B grain refiner was examined.

4.2.4.1 Microstructure of Al-Ti-B Grain Refined AZ91D Mg Alloy

Figures 4-35 and 4-36 show the general microstructure of the Al-Ti-B refined castings at both mold temperatures. Comparing the Al-Ti-B refined castings to the unrefined castings, significant grain size reduction was observed. Additionally, the grain boundaries in the Al-Ti-
B refined castings were surrounded by the eutectic phase, suggesting an improved distribution of the eutectic. The Al-Mn precipitates were not easily observable in the Al-Ti-B refined AZ91D Mg alloy in comparison to the unrefined alloy (Figure 4-29 to 4-30). Examining the effect of the additive concentration in the grain refiner revealed that the β-phase in the low concentration Al-Ti-B (i.e., Al-5Ti-1B) refined castings was more homogenously dispersed throughout the microstructure than in the high concentration refined casting, where clearly visible grain boundaries denuded of the eutectic phase were observed. Also, in the high concentration grain refiner, isolated colonies of the eutectic phase were frequently observed throughout the microstructure.

Figure 4-35: Microstructure of AZ91D Mg alloy refined with (a) Al-5Ti-1B and, (b) Al-15Ti-3B refiners, cast at 325 °C mold temperature.

Figure 4-36: Microstructure of AZ91D Mg alloy refined with (a) Al-5Ti-1B and, (b) Al-15Ti-3B refiners, cast at 300 °C mold temperature.
Addition of the Al-5Ti-1B grain refiner produced a grain size of ~60 μm and ~73 μm for the 325 °C and 300 °C mold temperatures, respectively. In the case of the Al-15Ti-3B grain refiner, the grain size was ~75 μm and ~74 μm for the two mold temperatures, respectively. Thus, for practical industrial considerations, the effect of the mold temperature on the grain size in the Al-Ti-B treated alloys was negligible.

Figure 4-37 shows the microstructure of the AZ91D Mg alloy treated with the commercially available Al-5Ti-1B refiner. In addition to the relatively larger grains, isolated regions of eutectic β-phase were also observed on the grain boundaries.

![Microstructure of AZ91D Mg alloy refined with commercial Al-5Ti-1B, cast at 325 °C mold temperature.](image)

The commercial Al-Ti-B refiner was not as effective as the SPS fabricated Al-Ti-B grain refiners. Also, the distribution of eutectic phase in the commercial Al-Ti-B refined alloy was similar to the unrefined alloy. Since the distribution of the low-melting temperature eutectic phases is often related to the interdendritic feeding during the late stages of solidification, these results suggest that the commercially refined alloy did not likely experience enhanced interdendritic feeding during the late stages of solidification.
4.2.4.1.1 Eutectic Phase

Figure 4-38 to 4-41 shows the eutectic phase for the Al-Ti-B refined castings. The Al-5Ti-1B refined castings at both mold temperatures showed a relatively more fully divorced eutectic. Furthermore, the microstructure shows long connected paths of divorced eutectic phase along the grain boundaries, often progressing towards the outer surface of the casting. Conversely, the eutectic phase in the Al-15Ti-3B refined castings was partially divorced with some lamella. It is expected that this multi-phase eutectic liquid present near the end of solidification would have a higher viscosity than the single-phase eutectic observed in the Al-5Ti-1B grain refined casting.

Published literature on the effect of Ti addition to AZ91 Mg alloys suggests that the transition from lamellar to fully divorced eutectic may occur if the Al concentration is locally varied [118]. If Al diffusion within the α-Mg matrix is reduced (i.e., reduced Al segregation to the grain boundaries), the lamellar eutectic formation may be suppressed. Therefore, based on Figure 4-38 to 4-41, the Ti from the Al-Ti-B refiners likely supported the suppression of lamella, or increased divorced eutectic formation.

Figure 4-38: Eutectic of the AZ91D Mg alloy refined with Al-5Ti-1B, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.
Figure 4-39: Eutectic of the AZ91D Mg alloy refined with Al-15Ti-3B, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-40: Eutectic of the AZ91D Mg alloy refined with Al-5Ti-1B, cast at 300 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-41: Eutectic of the AZ91D Mg alloy refined with Al-15Ti-3B, cast at 300 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-42 shows the eutectic phase of the AZ91D Mg alloy refined with the commercial Al-5Ti-1B. Figure 4-42a and 4-42b show the microstructure at the center and at the surface of...
the hot tear region, respectively. The eutectic in center region could be described as lamellar/fibrous with partially divorced islands at the grain boundaries. Near the casting surface, the eutectic phase along the grain boundaries is missing, suggesting poor liquid mobility near the end of solidification. However, the enrichment of Al in the interdendritic regions is observable, as evidenced by the fibrous/lamellar eutectic.

Figure 4-42: Eutectic phase in the AZ91D Mg alloy refined with commercial Al-5Ti-1B, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

4.2.4.2 Microstructure of Al-Ti-C Grain Refined AZ91D Mg Alloy

Figures 4-43 and 4-44 show the microstructure of the AZ91D Mg alloy refined with the Al-Ti-C grain refiners. Similar as in the case of the Al-Ti-B refiners, both Al-Ti-C grain refiners resulted in a more homogeneous distribution of the eutectic phase throughout the microstructure. The Al-Mn and Mg2Si precipitate formation in both Al-Ti-C refined AZ91D Mg alloys was similar to the precipitate formation in the unrefined AZ91D Mg alloy.
The grain size reduction achieved by the Al-5.4Ti-0.6C refiner at 325 °C and 300 °C mold temperatures was ~68% and ~65%, respectively. The Al-16.2Ti-1.8C refiner achieved a reduction of ~64% for both moth temperatures.

Successful grain refinement with TiC-based grain refiners was initially reported for Al alloys, while similar success has not been observed in Mg alloys. This may be due to the wettability of TiC by Al vs. TiC by Mg. According to Contreras et al. [64], Al has been observed to wet TiC at temperature from 800-1000 °C, while Mg was only able to wet TiC above 900 °C [64]. Contreras et al. [64] determined successful wetting to be a function of a mutual chemical bond based on valences between the liquid and solid phases at the onset of alloy solidification. The work by Han et al. [65] on grain refinement of AZ31 Mg alloy by TiC...
particles did result in appreciable grain refinement. Conversely, other literature suggests that TiC has been successful at providing grain refinement of Mg alloys [24], [62], [63], due to a combination of heterogenous nucleation, growth restriction, or a reaction with Al to form Al₄C₃, which was suggested to be an effective nucleant (as discussed in Section 2.2.2.2.2).

4.2.4.2.1 Eutectic Phase

Figures 4-45 to 4-48 show the eutectic phases in AZ91D Mg alloy refined with the Al-Ti-C grain refiner. The morphology of the eutectic phase was similar for all castings refined with Al-Ti-C formulations, described as partially divorced with some lamella. Many islands of divorced eutectic were observed along the grain boundaries. Additionally, some instances of fully divorced eutectic were noted.

![Figure 4-45: Eutectic of the AZ91D Mg alloy refined with Al-5.4Ti-0.6C, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.](image)
Figure 4-46: Eutectic of the AZ91D Mg alloy refined with Al-16.2Ti-1.8C, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-47: Eutectic of the AZ91D Mg alloy refined with Al-5.4Ti-0.6C, cast at 300 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-48: Eutectic of the AZ91D Mg alloy refined with Al-16.2Ti-1.8C, cast at 300 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.
4.2.4.3 Microstructure of Al-C Grain Refined AZ91D Mg Alloy

Figures 4-49 and 4-50 show the microstructure of the AZ91D Mg alloy refined with Al-2C and Al-10C grain refiners. The morphology and phases present in castings refined with this grain refiner were comparable to castings refined with the Al-Ti-B grain refiner. Compared to the unrefined AZ91D Mg alloys shown in Figure 4-30 to 4-32, the Al-Mn precipitate size appeared to be finer and more evenly dispersed for each AZ91D Mg alloy refined with the Al-C refiners. The grain size reduction in the AZ91D Mg alloy due to the Al-2C and Al-10C refiner was ~76% and ~72%, respectively, for both mold temperatures.

![Figure 4-49: Microstructure of AZ91D Mg alloy refined with (a) Al-2C and, (b) Al-10C, cast at 325 °C mold temperature.](image)

![Figure 4-50: Microstructure of AZ91D Mg alloy refined with (a) Al-2C and, (b) Al-10C, cast at 300 °C mold temperature.](image)
In the Al-2C refined AZ91D Mg alloy cast at 325 °C mold temperature, a homogeneous eutectic distribution along the grain boundaries was observed. This was likely due to the reduced carbon particle agglomeration in the Al-2C refiner, as compared to the Al-10C refiner, as previously discussed in Section 4.1.3. This possibly provided more individual de-agglomerated particles for inoculation of the melt.

Increasing the carbon content in the Al-C refiner had no further grain refining effect and even caused to slight grain coarsening, which has been observed in some literature [48], [49]. This effect was often attributed to carbon particle agglomeration due to the van der Waals forces of attraction between the individual carbon particles [49], [120]. With the increased concentration, agglomerations likely increased.

As discussed in the literature review, carbon has been suggested to react with the Al in the Mg alloy, producing either \( \text{Al}_2\text{C}_3 \) or \( \text{Al}_2\text{MgC}_2 \), both of which have been proposed as good nucleants for the \( \alpha \)-Mg phase [26], [34], [35], [41], [60], [62], [69]. Proof of these phases in the present research was not found and so evidence of the exact phase responsible for C-based grain refinement remains unclear.

### 4.2.4.3.1 Eutectic Phase

The effect of adding the Al-2C and Al-10C grain refiners on the AZ91D Mg alloy’s eutectic phase can be seen in Figures 4-51 to 4-54. A lamellar, partially divorced, and fully divorced eutectic morphologies were observed.
Figure 4-51: Eutectic of the AZ91D Mg alloy refined with Al-2C, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-52: Eutectic of the AZ91D Mg alloy refined with Al-10C, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-53: Eutectic of the AZ91D Mg alloy refined with Al-2C, cast at 300 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.
Figure 4-54: Eutectic of the AZ91D Mg alloy refined with Al-10C, cast at 300 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

The AZ91D Mg alloy refined with both Al-C refiners showed relatively long and thin branches of the eutectic phase along the grain boundaries, suggesting that the eutectic liquid was able to effectively feed in the final stages of solidification. As discussed later in Section 4.4.1.2.3, hot tearing was drastically reduced when this grain refiner was used, and thus the effectiveness of the feeding during the late stages of solidification was possibly a significant factor on the alloy’s hot tearing susceptibility.

4.2.4.4 Microstructure of Al-Ti Grain Refined AZ91D Mg Alloy

Figures 4-55 and 4-56 show the microstructure of the AZ91D Mg alloy refined with Al-Ti at various mold temperatures. In the Al-Ti refined castings, the eutectic was evenly dispersed along the grain boundaries. As discussed previously, a better eutectic distribution is often associated with improved interdendritic feeding during solidification. Additionally, all AZ91D Mg alloys refined with the Al-Ti grain refiner (in comparison to the unrefined AZ91D Mg alloy in Section 4.2.3) appeared to have a visibly reduced porosity.
Figure 4-55: Microstructure of AZ91D Mg alloy refined with (a) Al-6Ti and, (b) Al-18Ti, cast at 325 °C mold temperature.

Figure 4-56: Microstructure of AZ91D Mg alloy refined with (a) Al-6Ti and, (b) Al-18Ti, cast at 300 °C mold temperature.

The average reduction in grain size due to the Al-6Ti grain refiner addition to the AZ91D Mg alloy was ~78% at both mold temperatures. The Al-18Ti grain refiner produced an average reduction of ~80%, at both mold temperatures.

Figure 4-57 shows a Ti particle within the primary Mg phase. The Ti particle has several grains growing from its surface, thus suggesting that the particle itself was possibly a substrate for heterogenous nucleation of primary Mg grains. From the linescan in Figure 4-57b, some diffusion of Ti has occurred into the primary phase around the Ti particle, suggesting that a good wettability enabled coherent bonding between the primary Mg phase and the particle. Additionally, a concentration increase in Al content was observed at the particle boundary, which likely corresponded to the intermediate layer observed in the Al-Ti
refiners. The TiAl$_3$ was present in the XRD patterns for the Al-18Ti refiner, which could be the intermetallic phase enabling enhanced nucleation.

![Image of Ti particle map and linescan]

**Figure 4-57**: XEDS (a) map and (b) linescan across a Ti particle in the Al-18Ti refined casting at 325 °C mold temperature; Mg denoted by red line, Al denoted by blue line, Ti denoted by orange line.

### 4.2.4.4.1 Eutectic Phase

Figures 4-58 to 4-61 show the effect of the Al-Ti grain refiner on the AZ91D Mg alloy's eutectic phase. The Al-6Ti and Al-18Ti refiners have produced a fully divorced eutectic at both mold temperatures. Long branches of fully divorced eutectic were often seen across the microstructure and were seen to span numerous Mg grains.
Figure 4-58: Eutectic of the AZ91D Mg alloy refined with Al-6Ti, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-59: Eutectic of the AZ91D Mg alloy refined with Al-18Ti, cast at 325 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Figure 4-60: Eutectic of the AZ91D Mg alloy refined with Al-6Ti, cast at 300 °C mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.
Figure 4-61: Eutectic of the AZ91D Mg alloy refined with Al-18Ti, cast at 300 ºC mold temperature; (a) Center of critical hot tear region, (b) Near hot tear at casting surface.

Ti additions have been reported in the literature to produce fully divorced eutectic morphology [118]. The effect of Ti has been related to grain growth restriction of the α-Mg phase during solidification and has been observed to prevent diffusion of Al out of the Mg matrix, as reported by Candan et al. [121]. With the Ti addition, transformation of the eutectic from lamellar and partially divorced to fully divorced was achieved.

4.3 Diffraction Analysis

Several diffraction-based analyses were carried out in this research to further the understanding of the fundamental mechanisms involved in the grain refinement in the AZ91D Mg alloy with the newly prepared grain refiners.

4.3.1 X-Ray Diffraction of AZ91D Mg Alloy

Figures 4-62 and 4-63 show the diffraction patterns for all castings made at 325 ºC mold temperature. The XRD analysis of the refined AZ91D Mg alloy showed no additional or new phases evolving as a result of the grain refinement, suggesting that the grain refining additives did not transform in appreciable amounts and did not form new phases in appreciable quantities. It is recognized, however, that given the low addition amounts of the
grain refiners, the volume fraction of the refiner particles, or the potential phases described earlier in Section 2.2.2.2, were likely below the minimum detectability limit of the XRD instrument.

Figure 4-62: XRD patterns of AZ91D Mg alloy refined with low concentration refiners, cast at 325 °C mold temperature.
Figure 4-63: XRD patterns of AZ91D Mg alloy refined with high concentration refiners, cast at 325 °C mold temperature.

A difference in the XRD patterns for the unrefined and refined AZ91D Mg alloys was observed in the α-Mg matrix peak corresponding to the (0002) basal plane (2θ of ~35°). The larger intensity of the basal peak in the unrefined AZ91D Mg alloy may indicate a higher volume fraction of grains with this crystallographic orientation. In the case of the refined AZ91D Mg alloy, the peak intensity for the basal planes was reduced and remained comparable for the various grain refiners studied. An exception to this was in the case of the AZ91D Mg alloy treated with the commercial Al-5Ti-1B refiner. The commercial Al-5Ti-1B refined alloy showed a larger basal plane peak intensity, similar to the unrefined alloy.
Comparing the unrefined AZ91D Mg alloy pattern to a pattern from a fine-grained AZ91D Mg alloy powder pattern produced by Taleghani et al. [122], the {000\ 2} reflection was significantly larger in the unrefined alloy in this research. In contrast, comparing the XRD patterns for the grain refined AZ91D Mg alloys to the powdered AZ91D Mg alloy from Taleghani et al. [122], the peak intensities in the present work were comparable to the randomly oriented powdered AZ91D Mg alloy. This result indicates that the grain refined alloys likely had a more random grain orientation [29], which was further studied via EBSD crystallographic analysis.

### 4.3.2 Electron Back Scatter Diffraction of AZ91D Mg Alloy

Directionally solidified castings often exhibit undesirable crystallographic texture. In the present work, the heat transfer in the horizontal bar was predominantly in the axial direction (i.e., directional solidification from the end of the horizontal bar towards the downsprue). To study the impact of the solidification directionality on the grain's crystal orientation, EBSD mapping was carried out near the hot tear region.

#### 4.3.2.1 Texture Grain Maps

EBSD analysis was carried out near the hot tear region castings completed at the 325 °C mold temperature. Maps were generated along a line from the center of the horizontal bar towards the mold interface. Figures 4-64 to 4-68 show the EBSD grain maps of the unrefined AZ91D Mg alloy and the alloy refined with the Al-5Ti-1B, Al-5.4Ti-0.6C, Al-2C, and Al-6Ti.
Figure 4-64: EBSD grain map of unrefined AZ91D Mg alloy, cast at 325 °C mold temperature.

Figure 4-65: EBSD grain map of AZ91D Mg alloy refined with Al-5Ti-1B, cast at 325 °C mold temperature.

Figure 4-66: EBSD grain map of AZ91D Mg alloy refined with Al-5.4Ti-0.6C, cast at 325 °C mold temperature.

Figure 4-67: EBSD grain map of AZ91D Mg alloy refined with Al-2C, cast at 325 °C mold temperature.

Figure 4-68: EBSD grain map of AZ91D Mg alloy refined with Al-6Ti, cast at 325 °C mold temperature.

The EBSD grain maps and grain size results were in good agreement with the results of optical microscopy in Section 4.2.4 (microstructure of refined castings). It is evident that a significant grain size reduction was achieved with each SPS prepared grain refiner. Except
for a few large grains, the refined castings had a more uniform grain morphology across the entire scan area (i.e., from the center of the horizontal bar towards the metal-mold interface). In the unrefined AZ91D Mg alloy, the grain size was larger in the center of the horizontal bar as compared to the metal-mold interface region. In contrast, in each refined alloy (Figure 4-65 to 4-68), the center and surface regions had similar grain size and morphology, which is consistent with the analysis completed in Section 4.2.1.1.

### 4.3.2.2 Pole Figures

Figures 4-69 to 4-73 show representative pole figures for the unrefined AZ91D Mg alloy and the alloy refined with the Al-5Ti-1B, Al-5.4Ti-0.6C, Al-2C, and Al-6Ti, cast at 325 °C mold temperature. The {0001}, {11-20}, and {10-10} projections were used to display the data.

**Figure 4-69**: EBSD pole figure of unrefined AZ91D Mg alloy, cast at 325 °C mold temperature.

**Figure 4-70**: EBSD pole figure of AZ91D Mg alloy refined with Al-5Ti-1B, cast at 325 °C mold temperature.
In the case of the unrefined AZ91D Mg alloy, a slightly non-uniform distribution was observed with an MUD of 7.7. Conversely, the Al-5Ti-1B, Al-5.4Ti-0.6C, Al-2C and Al-6Ti refined alloys had a more random distribution and a lower MUD of 3.13, 3.41, 2.49, and 2.73; respectively. The unrefined alloy likely had a larger MUD due to larger grains. A large grain in one orientation will contribute greater intensity of that orientation to the overall
projection. To conclusively quantify the effect of the grain refiners on texture, however, further investigation is required.

4.3.3 Neutron Diffraction of AZ91D Mg Alloy

The application Neutron Diffraction (ND) in this research provided a unique opportunity for in-situ analysis of the grain refined AZ91D Mg alloys during solidification.

4.3.3.1 Microstructure

The microstructure of the samples analyzed via ND can be observed in Figures 4-74 to 4-76. The phases present in the alloy after ND analysis were comparable to the phases present in the AZ91D steel mold castings. Due to the slower cooling rate of the alloy to room temperature during ND experiments, the volume fraction of the lamellar eutectic β-phase along the grain boundaries increased. Formation of this lamellar phase is achieved during solid-state phase transformation of the super-saturated α-Mg upon cooling.

Comparing the micrographs in Figure 4-74 to 4-76 with the micrographs from as-cast AZ91D Mg alloy (Section 4.2), it is evident that the grain size in the ND samples was larger than in the steel mold cast alloy. Again, this was likely the result of the slow cooling of the AZ91D Mg alloy during ND experiments, which likely enabled extended growth during solidification. The impact of extended grain growth after completion of solidification may have also affected the final grain size, which likely hindered comparison of grain size in the refined AZ91D Mg alloy samples.
Figures 4-74 to 4-76 reveal that the morphology of the eutectic phase changed towards a fully divorced eutectic in the case of the refined alloys. In the unrefined alloy, the eutectic phase was primarily a partially divorced or fibrous eutectic. The change in the eutectic morphology of the grain refined alloys suggests an improvement in fluidity of the liquid at the eutectic composition near the end of solidification.

The microstructure of the unrefined and refined alloys subjected to ND experiments was analyzed via XEDS linescan analysis. Figure 4-77 shows a representative linescan...
spanning a grain boundary and the eutectic region. Based on XEDS analysis of 50 grains per alloy sample, the concentration of Al in the unrefined AZ91D Mg alloy was ~2% lower than in the Al-Ti-C and Al-C refined alloys (6.40 ± 0.40 wt%, 8.40 ± 0.70 wt%, 8.41 ± 0.80 wt% of Al in the grains of the unrefined, Al-Ti-C refined, and Al-C refined alloys, respectively). Focusing on the Al content (blue line), the linescans show that the unrefined AZ91D Mg alloy had a greater variation of Al concentration (between 3 wt% - 12wt%) across the grains as compared to the refined alloys (between 9 wt% - 13wt%). This coring effect is typically the result of non-equilibrium solidification, with the liquid phase having non-uniform solute concentration [5]. In the case of the Al-Ti-C and Al-C refined alloys, the more consistent Al concentration in the grains suggests a more uniform liquid phase concentration, likely the result of enhanced diffusion of Al into the α-Mg phase as a result of the increased surface area (and shorter diffusion lengths) in the refined castings.

![XEDS Linescans from centers of neighbouring grains through the eutectic region for AZ91D Mg alloy](image)

**(a)** (b) (c)

*Figure 4-77: XEDS Linescans from centers of neighbouring grains through the eutectic region for AZ91D Mg alloy; (a) unrefined, (b) Al-Ti-C refined, (c) Al-C refined; Mg denoted by red line, Al denoted by blue line, Zn denoted by green line.*

### 4.3.3.2 Diffraction Patterns

During the ND in-situ solidification experiments, the diffraction peaks corresponding to the α-Mg and β-Mg$_{17}$Al$_{12}$ phases of the AZ91D Mg alloy were tracked. Figures 4-78 to 4-80 show
the evolution of the ND patterns of the unrefined, Al-Ti-C refined, and Al-C refined alloys during cooling from 630°C to 40°C with each peak labelled with the corresponding phase. Each pattern in the 3D stack plot has been made relative to the most intense peak of all patterns to reduce the high intensity background created by diffuse scattering and the Debye-Waller effect (also known as temperature factor) [29]. Diffuse scattering is caused by the random interaction of neutrons with the molten metal contributing to the background in the diffraction pattern. The Debye-Waller effect occurs in the solid structure at high temperatures due to the thermal motion of the atoms, as previously explained in section 3.5.3.3. Together, the relative 3D stack plot representation allows the elastic scattering of the solid phase to be well defined across each temperature step.

The observed increase in the peak intensities in the ND patterns corresponds to the increase in the fraction of solids of respective phases, as discussed previously in Section 3.5.3.3. The observed peak shifts towards higher diffraction angles as the temperature decreased was related to the thermal contraction of the α-Mg crystal lattice.
Figure 4-78: Diffraction patterns collected during solidification of unrefined AZ91D Mg alloy for angles (a) 49° to 60°, and (b) 74° to 110°.
Figure 4-79: Diffraction patterns collected during solidification of AZ91D Mg alloy refined with Al-Ti-C, for angles (a) 49° to 60°, and (b) 74° to 110°.
Figure 4-80: Diffraction patterns collected during solidification of AZ91D Mg alloy refined with Al-C, for angles (a) 49° to 60°, and (b) 74° to 110°.

Prior to the onset of solidification (at ~630°C), no peaks were detected by ND, confirming that the sample was completely liquid. As temperature started to decrease, ND confirmed the theoretical liquidus of AZ91D Mg alloy to be ~595°C, which is consistent with literature [38], [99]. As Figures 4-78 to 4-80 show, at 593°C the {10-11} reflection appeared as a low intensity peak due to the small fraction of crystalline Mg. As cooling continued below 593°C, additional peaks, such as the {10-10} and {0002} reflections appeared. For all reflections, the peak intensity increased with progressing solidification and increase of the solid phase in the material. At 440-430 °C, the increase of the peak intensities for each {hkil} plane
appeared to temporarily arrest, indicating the end of solidification. Based on the ND results, the end of solidification for the unrefined alloy occurred between 440 °C and 435 °C, while the measured solidus temperature for the refined alloys was found to be ~435-430 °C. The β-Mg$_{17}$Al$_{12}$ phase in the unrefined and refined alloys was detected via the {330} reflection [99]. Both refined alloys exhibited the β-Mg$_{17}$Al$_{12}$ peak at ~430 °C, while the unrefined alloy exhibited the β-Mg$_{17}$Al$_{12}$ peak at ~405 °C. As discussed in Section 4.3.3.1, the refined alloys had a greater amount of a fully divorced eutectic, which is in agreement with the ND results. In the case of the unrefined AZ91D Mg alloy, the lamellar β-phase formed mainly through solid-state precipitation after solidification was completed, which was observed in micrographs in Section 4.3.3.1.

4.3.3.3 Fraction of Solid Curves

Figure 4-81 shows the Fraction of Solid (FS) curves for the α-Mg for the unrefined, and Al-Ti-C and Al-C refined AZ91D Mg alloy samples subjected to ND experiment. The estimate of uncertainty based on the 95% confidence interval was 0.01 for all FS values.
Figure 4-81: Fraction of Solid curves of the α-Mg phase for unrefined and refined AZ91D Mg alloys.

The FS curves revealed a visible slope change (i.e., rate of fraction of solid evolution) during solidification. In the unrefined alloy, the curve slope was steeper and reached a higher fraction of solid (>0.9) approximately 30 – 40°C earlier than in the case of the refined alloys. The fraction of solid curves for all alloys were comparable until ~575°C, at which point the curves for the unrefined and refined alloys began to diverge. This temperature corresponds to the end of nucleation of the α-Mg phase. After this temperature, the refined alloys were consistently at a lower fraction of solid until the end of solidification, suggesting that a higher volume fraction of liquid was available following the dendrite coherency point. A greater volume fraction of liquid would improve interdendritic feeding at late stages of solidification,
which likely influenced the refined alloy’s hot tearing susceptibility, as will be discussed in Section 4.4.

Figure 4-82 shows the evolution of the $\beta$-Mg$_{17}$Al$_{12}$ phase for each alloy near the end of solidification and subsequent cooling to room temperature. The reported fraction of solid was based on the intensity of the \{330\} crystallographic reflection and includes the interdendritic eutectic phase as well as the lamellar (solid-state) eutectic phase.

![Figure 4-82: Fraction of Solid curves of the $\beta$-Mg$_{17}$Al$_{12}$ for unrefined and refined AZ91D Mg alloys.](image)

Figure 4-82 shows that in the Al-C and Al-Ti-C refined AZ91D Mg alloy, most of the $\beta$-phase volume fraction formed immediately at the end of solidification. This may suggest most of the remaining liquid at the end of solidification was at the eutectic composition. This low melting temperature eutectic liquid was available to feed the interdendritic channels of the
primary phase in the refined alloys. This would have resulted in enhanced feeding, which is further supported with the microstructure analysis where a divorced eutectic was observed in the refined AZ91D Mg alloys.

Further analysis of the diffraction patterns has provided quantitative analysis of the weight fractions of each phase during solidification. Rietveld refinement was used (Figure 4-83) to plot the weight percent of each phase in the alloy during cooling to room temperature.

![Fraction of Solid curves showing the corresponding weight percent of α-Mg and β-Mg_{17}Al_{12} for the unrefined and refined AZ91D Mg alloys.](image)

The quantitative Rietveld analysis shows that the weight fraction of the β-Mg_{17}Al_{12} phase in both grain refined alloys was ~2 wt% lower at the room temperature (40 °C) than in the unrefined AZ91D Mg alloy (9.0 ± 0.336 wt%, 7.0 ± 0.321 wt%, and 6.9 ± 0.331 wt% of β-Mg_{17}Al_{12} phase for unrefined, Al-Ti-C refined, and Al-C refined, respectively). This reduction
was observed despite the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phases higher weight fraction at higher temperatures in both the refined alloys. This result likely indicates more Al remained in the $\alpha$-Mg solid solution in the grain refined AZ91D Mg alloys. This is further supported with previously discussed XEDS chemical analysis (Section 4.3.3.1), where the Al solid solution content in the $\alpha$-Mg phase was higher in the grain refined AZ91D Mg alloys than the unrefined AZ91D Mg alloy. Furthermore, literature suggests the presence of a fully divorced eutectic, observed in Figure 4-75 and 4-76, is consistent with an increased Al concentration in the $\alpha$-Mg phase (i.e., less Al available for $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase, forcing a fully divorced morphology) [98], [118], [121].

4.4 Analysis of Hot Tearing

The following Section provides quantitative results of hot tear analysis using the instrumented permanent mold. The results of in-situ force and temperature analysis and its relation to the severity of hot tearing are presented.

4.4.1 Hot Tearing of AZ91D Mg Alloy

The hot tear severity for all castings was intentionally examined at the onset of hot tearing. Several experiments were performed at a low mold temperature, where a severe hot tear formed. Since such castings had a fully developed crack that would deem such a casting as a scrap in industrial applications, the corresponding low mold temperature were not explored further. In contrast, above 350 °C mold temperatures (cooling rate less than 1 °C/s), hot tears were eliminated in the unrefined and refined alloys. As a result, special focus was given to castings produced at mold temperatures from 300 - 325 °C, where initiation of hot tears was readily observed at the 90° junction between the horizontal bar and the downsprue.
4.4.1.1 Hot Tearing of Unrefined AZ91D Mg Alloy

Figure 4-84 shows representative hot tears in the unrefined AZ91D Mg alloy cast at mold temperatures from 300 °C to 350 °C (cooling rate varied from 4 to 1 °C/s). The hot tear severity decreased consistently with increasing mold temperature.

The observed hot tears propagated radially towards the interior of the casting uniformly around the circumference of the horizontal bar at the 90° stress concentration. Since a uniform hot tear formed on the exterior of the horizontal bar along its circumference, the formation of ~2 mm deep hot tear would have a significant impact on the load bearing capacity of the horizontal bar (which had an original 6 mm radius). Therefore, a relatively minor hot tear would compromise the integrity of the casting.

At the 350 °C mold temperature, hot tears were eliminated, as seen in Figure 4-84a, despite a few pores visible at the typical hot tear nucleation region. Figure 4-84b shows that at 325 °C mold temperature, a hairline hot tear approx. 0.8-1.0 mm long was present. This
condition was termed as the onset of hot tearing. The hairline hot tear propagated from the surface of the casting at the stress concentration diagonally towards the casting interior in the direction of the maximum stress gradient. At the 300 °C mold temperature (Figure 4-84c), the hot tear length significantly increased to ~1.8-2.0 mm. Additionally, the alloy cast at the 300 °C mold temperature shows a smoother crack interface as compared to the alloy cast 325 °C mold temperature. This suggests the tear in the lower mold temperature casting occurred at an earlier stage of solidification (i.e., high temperature and lower fraction of solid) [17], [40], which correlates with results observed in Section 4.4.2.

4.4.1.1.1 Hot Tear Morphology

In the present research, all hot tears nucleated at the stress-concentration region (i.e., a 90° junction between the horizontal bar and the downsprue) and propagated via grain boundaries in the direction of decreasing stress gradient, as seen in Figure 4-84. With this type of hot tear propagation, high grain density may increase the hot tearing resistance as the tear would have to propagate through a complex network of grain boundaries. Furthermore, smaller grains may impinge upon each other at a later stage in solidification which would allow transfer of solidification stress and its dissipation away from the stress concentration [21].

In contrast, the grain size reduction could also negatively impact hot tearing, since an increase in surface grain area (where the low melting temperature eutectic phase resides) could facilitate grain boundary sliding at elevated temperatures (i.e., near the end of solidification). Such grain boundary sliding could result in enhanced hot tearing [9], [14], [18], [28]. Therefore, elimination of hot tears via grain refinement is a complex interplay of competing factors.

Figure 4-85 shows the differences in the surface morphology between the hot tears observed in the 325 °C and 300 °C mold temperature castings (cooling rates of 1.5 to 2.5
0°C/s and 3.0 to 4.0 ⁰C/s, respectively). At the 325 ⁰C mold temperature, the hot tear had a rough surface and each side of the tear with mating features. Such a crack morphology indicates the evolution of a tensile strain on the hot tear and also the absence of a liquid phase in the hot tear region. In the case of the casting produced at 300 ⁰C mold temperature, a smooth tear morphology without mating surfaces was observed, suggesting that a liquid phase was mobile during the late stages of solidification when the hot tear was forming. It is likely, that the liquid phase was able to heal the incipient hot tear.

Figure 4-85: Critical hot tear region showing an intergranular tear path in the AZ91D Mg alloy, cast at (a) 325 ⁰C, and (b) 300 ⁰C mold temperature.

4.4.1.2 Hot Tearing of Grain Refined AZ91D Mg Alloy

The following text provides a discussion of the hot tear severity and tear morphology of the refined AZ91D Mg alloy castings. When suitable, a comparison to the unrefined AZ91D Mg alloy castings are presented.

4.4.1.2.1 Hot Tearing of Al-Ti-B Grain Refined AZ91D Mg Alloy

Figure 4-86 shows representative hot tears observed in the AZ91D Mg alloy refine with the Al-Ti-B, cast at the 325 ⁰C mold temperature. The hot tear spanned several dendritic grains and reached ~0.6 mm into the casting interior from the casting surface (refer to Appendix D...
for dendritic structure within grains of as-cast AZ91D). In the Al-5Ti-1B grain refined casting, the micro hot tear only formed on the surface and remained as a surface defect. In the Al-15Ti-3B grain refined casting, the discontinuous micro hot tear was observed in two segments, which lined-up parallel to the downsprue. The hot tears in the Al-Ti-B castings were only visible with a microscope.

Figure 4-86: Critical hot tear region of casting refined with (a) Al-5Ti-1B, and (b) Al-15Ti-3B, cast at 325 °C mold temperature.

Figure 4-87 shows that at the 300 °C mold temperature, the severity of hot tears increased in comparison to the 325 °C mold temperature casting. For the AZ91D Mg alloy refined with Al-5Ti-1B grain refiner, a ~0.4 mm long hot tear was visible near the casting exterior but did not appear to extensively propagate towards the casting interior. Figure 4-87b shows that with a further increase of the grain refiner concentration, the hot tear was no longer continuous and instead formed a bridge between the porosity-like voids. This morphology was possibly the result of the eutectic liquid flow feeding the evolving tear during solidification.
The present results indicate that the refined alloy retained mobile eutectic liquid for a longer period, despite the higher cooling rates recorded during solidification as compared to the unrefined alloy. Interdendritic liquid feeding also reduced formation of shrinkage porosity, which is frequently considered the initial stage of hot tear development. These observations are further supported by the *in-situ* force evolution measurements during casting solidification, which will be discussed in Section 4.4.1.2.1.

Although the commercial Al-5Ti-1B refiner showed some grain size reduction, it did not result in a significant hot tear reduction, as observed in Figure 4-88. The length of the hot tear remained at ~0.8-1.0 mm. Additionally, the tear was discontinuous, suggesting that multiple tears nucleated and likely joined together. Furthermore, a portion of the tear was parallel to the direction of the constrained rod (i.e., direction of the tensile load due to shrinkage). This suggests that a portion of the hot tear propagated due to shear as well as tensile loading in the critical casting region. The lower Section of the hot tear region appears
to have a segment that was back-filled with eutectic phase; however, the amount of eutectic liquid was insufficient to completely close the hot tear, and the tip of the hot tear remained as a void.

Figure 4-88: Critical hot tear region of casting refined with commercial Al-5Ti-1B, cast at 325 °C mold temperature.

4.4.1.2.2 Hot Tearing of Al-Ti-C Grain Refined AZ91D Mg Alloy

Figure 4-89 shows representative hot tears for the Al-Ti-C grain refined castings produced at the 325 °C mold temperature. The Al-5.4Ti-0.6C refined casting had a hot tear ~0.35-0.4 mm long, while the higher concentration grain refiner (Al-16.2Ti-1.8C) caused a ~0.6 mm long hot tear with a visible increase in micro-porosity in the hot tear tip vicinity.
Figure 4-89: Critical hot tear region of casting refined with (a) Al-5.4Ti-0.6C, and (b) Al-16.2Ti-1.8C, cast at 325 °C mold temperature.

Figure 4-90 shows the hot tear severity in the grain refined castings produced at the 300 °C mold temperature. The length of the hot tears increased to ~1 mm for both castings. In the case of the AZ91D Mg alloy refined with Al-5.4Ti-0.6C in Figure 4-90a, the hot tear consisted of porosities and voids aligned in the direction of the maximum stress gradient. In the mid-span of the hot tear, the crack width significantly reduced and was nearly eliminated, indicating that liquid metal feeding at high fractions of solid was operative. However, the feeding was not sufficient to fully heal the interdendritic shrinkage porosity, as seen in the region just below the hot tear in Figure 4-90a (refer to Appendix D for dendritic structure within grains of as-cast AZ91D).
Figure 4-90b reveals that the hot tear in a casting refined with the Al-16.2Ti-1.8C refiner propagated in a “Z” pattern. This pattern of tear propagation suggests that the magnitude of the axial contractions of the horizontal bar and the downsprue, which were perpendicular to each other, were the dominant driving forces for the hot tear propagation. With decreasing temperature, the downsprue and horizontal bar contracted, with the greatest interference between these contractions observed at the 90° stress concentration. The primary hot tear, as well as secondary cracks visible in Figure 4-90b were nearly perfectly aligned at 45° to the axial contractions of the horizontal bar and the downsprue.

4.4.1.2.3 Hot Tearing of Al-C Grain Refined AZ91D Mg Alloy

Figure 4-91 shows hot tears in castings produced at 325 °C mold temperature and treated with the Al-2C and Al-10C refiners, respectively. Similar to the Al-Ti-B refined castings, the hot tear has been reduced to a surface porosity with both the Al-2C and Al-10C refiners. Additionally, there was no evidence of interdendritic shrinkage porosity in the castings.
Figure 4-91: Critical hot tear region of casting for AZ91D Mg alloy refined with (a) Al-2C, and (b) Al-10C, cast at 325 °C mold temperature.

Figure 4-92 shows as the mold temperature decreased to 300 °C, the hot tear severity rapidly increased. Bridges between cracks (e.g., Figure 4-92a, lower crack) were observed, indicating the presence of limited eutectic liquid near the end of solidification.
Interestingly, the location of the hot tear has shifted towards the upper portion of the 90° corner. This shift indicates that the solidification of the horizontal bar was completed prior to additional solidification of the downsprue. Consequently, opening of the hot tear was driven by the thermal contraction of the horizontal bar, rather than by the complementary (and simultaneous) shrinkage and contractions of the downsprue and the horizontal bar.

4.4.1.2.4 Hot Tearing of Al-Ti Grain Refined AZ91D Mg Alloy

The Al-6Ti and Al-18Ti refiners resulted in significant reduction of hot tearing, at both mold temperatures. Figure 4-93 shows that in the 325 °C mold temperature castings, hot tears were fully eliminated. Figure 4-94 shows the 300 °C mold temperature castings, where micro hot tearing was present only in the Al-6Ti refined AZ91D Mg alloy. Comparing all the refiners tested in this research, the Al-18Ti grain refiner has shown to be the most effective at reducing hot tearing and achieved one of the smaller grain sizes. The results in Figure 4-93 and 4-94 clearly illustrate the direct impact of grain size, grain homogeneity and the
availability of eutectic liquid on the ability to reduce and remove interdendritic porosity and hot tearing.

Figure 4-93: Critical hot tear region of casting refined with (a) Al-6Ti, and (b) Al-18Ti, cast at 325 °C mold temperature.

Figure 4-94: Critical hot tear region of casting refined with (a) Al-6Ti, and (b) Al-18Ti, cast at 300 °C mold temperature.
4.4.2 Force and Cooling Curves

The *in situ* force and temperature data collected during the metalcasting experiments provided quantitative information related to the solidification rate and the rate of force evolution in the horizontal bar. This data was subsequently used to compute the solidification kinetics of an alloy in relation to the observed severity of hot tearing.

4.4.2.1 Force and Cooling Curves for Unrefined AZ91D Mg Alloy

Table 4-3, 4-4 and Figure 4-95 show the *in situ* data for the unrefined AZ91D Mg alloy cast at 300 °C, 325 °C, 350 °C mold temperatures.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Total Solidification Time (s)</th>
<th>Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>139.5</td>
<td>1.1</td>
</tr>
<tr>
<td>325</td>
<td>105.5</td>
<td>1.5</td>
</tr>
<tr>
<td>300</td>
<td>48.5</td>
<td>3.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Force at Inflection (N)</th>
<th>Force at FS=1 (N)</th>
<th>Solidification Time after Inflection (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>8.5</td>
<td>62.2</td>
<td>120</td>
</tr>
<tr>
<td>325</td>
<td>30</td>
<td>70.1</td>
<td>91.5</td>
</tr>
<tr>
<td>300</td>
<td>55.4</td>
<td>77.5</td>
<td>36.5</td>
</tr>
</tbody>
</table>
The local solidification time and the cooling rate of each casting in Table 4.3 were computed using the theoretical solidification range. As expected, with increasing mold temperature the cooling rate decreased. At 350 °C mold temperature, no hot tearing was observed in the AZ91D Mg alloy. At this mold temperature, the casting solidified at ~1 °C/s. As the mold temperature decreased and hot tearing increased, the cooling rate increased to 1.5 °C/s and 3.2 °C/s for the 325 °C and 300 °C mold temperatures, respectively. Conversely, minimal grain size reduction due to decreased cooling rate via mold temperature was observed (Section 4.2.1) given the grain size of alloys known dependency on cooling rate [67], [83].

The force and temperature profiles present in this work are consistent with general trends reported in the literature for similar mold setups [14], [75], [28]. Each cooling curve in Figure 4-95a follows a similar profile without any thermal arrests or unexpected variations. The cooling curves decreased rapidly from liquidus to ~525 °C, which coincided with the formation of the \( \alpha \)-Mg solid solution phase. With additional latent heat release by the newly forming phase, and considering the effect of the mold temperature, the cooling rate slowed down and depending on the mold temperature, the subsequent cooling rate varied.

However, no new thermal arrests or plateaus were observed on any of the cooling curves.
The trend in the force curves (Figure 4-95b) reveals a rapid force increase approximately during the same period when the $\alpha$-Mg solid solution formed. This initial rapid increase in the force was also associated with the formation of a solid skin at the metal-mold interface, which coincided with the region of the highest heat transfer. This solid skin would be capable of sustaining and transferring load in the semi-solid casting.

As solidification progressed, dendritic network in the casting interior evolved and further contributed to the increasing force experienced by the casting horizontal bar (refer to Appendix D for dendritic structure within grains of as-cast AZ91D). As the alloy reached a high fraction of solid (>0.85), a gradual slope change in the force curve was observed. The force curves for the 325 °C and 300 °C castings show force fluctuations during solidification towards the end of the solidification range, at which point a large force relaxation was observed. This relaxation was an indication of a hot tear as the solidifying structure was likely unable to sustain the load developed due to shrinkage and propagated a hot tear to relieve it. This relaxation and its relation to hot tearing has been reported in the literature by several authors [7], [14], [28], [75], [92]. In the 300 °C mold temperature casting, a large force-drop of ~12N at the end of solidification was observed. In the case of the 325 °C mold temperature casting, a force drop of ~8 N was observed, nearly a 30% lower force magnitude. In the 350 °C casting, a monotonic increase in force was observed without force relaxation or fluctuation events.

Figure 4-95c compares the fraction of solid and force evolution during solidification. The key consideration in this plot is the magnitude of fraction of solid when the material began to sustain force. Theoretically, the higher the fraction of solid before appreciable magnitude of force develops, the lower the susceptibility of hot tear nucleation. In the present work, the instance of force evolution likely coincided with the tensile coherency or rigidity point of the solidifying structure. This is consistent with literature, where the tensile coherency fraction of solid for was reported to be ~0.6-0.8 in Mg alloys [75], [76]. The 350 °C mold temperature
casting shows that the force did not evolve until the casting was at a fraction of solid of ~0.82, while in the case of castings made at lower mold temperature, the force began to evolve at lower fraction of solids.

Data related to the force evolution is shown in Table 4-4. The results indicate that magnitude of force at the inflection and at the end of solidification, for each casting, increased with a decreased mold temperature. As it was previously shown in Section 4.4.1.1 for the unrefined AZ91D Mg alloy, increased cooling rate correlated with increased hot tear severity. Therefore, this result possibly suggests a quantitative relationship is present between the hot tearing severity and cooling rate via the force evolution.

Furthermore, most of the solidification time in the unrefined AZ91D Mg alloy occurred after the inflection in the load curves. As most of the solidification process, in terms of time, is spent at a high fraction of solid (>0.85), the significance of ensuring adequate liquid feeding to accommodate further shrinkage and hot tearing becomes apparent. Consequently, retaining a microstructure that would promote feeding would be crucial to provide resistance to hot tear nucleation.

4.4.2.2 Force and Cooling Curves for Grain Refined AZ91D Mg Alloy

The following text summarizes the in-situ force and temperature data collected during solidification of grain refined casting and compares the trends to the unrefined AZ91D Mg alloy castings.

4.4.2.2.1 Force and Cooling Curves for Al-Ti-B Grain Refined AZ91D Mg Alloy

Tables 4-5 and 4-6 and Figures 4-96 and 4-97 show the in-situ force and temperature data for the Al-Ti-B refined AZ91D Mg alloys, with a comparison to the unrefined AZ91D Mg alloy. The cooling data for the Al-Ti-B refined alloys showed no new exothermic deviations or arrests.
Table 4-5: Temperature Data for AZ91D Mg Alloy Refined with Al-Ti-B.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Total Solidification Time (s)</th>
<th>Average Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>105.5</td>
<td>1.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-5Ti-1B</td>
<td>68.5</td>
<td>2.3</td>
</tr>
<tr>
<td>325</td>
<td>Al-15Ti-3B</td>
<td>77</td>
<td>2.1</td>
</tr>
<tr>
<td>300</td>
<td>Unrefined</td>
<td>48.5</td>
<td>3.2</td>
</tr>
<tr>
<td>300</td>
<td>Al-5Ti-1B</td>
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<td>4.0</td>
</tr>
<tr>
<td>300</td>
<td>Al-15Ti-3B</td>
<td>44.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 4-6: Force Data for AZ91D Mg Alloy Refined with Al-Ti-B.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Force at Inflection (N)</th>
<th>Force at FS=1 (N)</th>
<th>Solidification Time after Inflection (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>30</td>
<td>70.1</td>
<td>91.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-5Ti-1B</td>
<td>35.4</td>
<td>61.7</td>
<td>50.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-15Ti-3B</td>
<td>40</td>
<td>65.6</td>
<td>61</td>
</tr>
<tr>
<td>300</td>
<td>Unrefined</td>
<td>55.4</td>
<td>77.5</td>
<td>36.5</td>
</tr>
<tr>
<td>300</td>
<td>Al-5Ti-1B</td>
<td>55.6</td>
<td>71.1</td>
<td>24.5</td>
</tr>
<tr>
<td>300</td>
<td>Al-15Ti-3B</td>
<td>63.2</td>
<td>73.1</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Figure 4-96: (a) Cooling, (b) Force, and (c) Fraction of solid v. Force curves for AZ91D Mg alloy refined with Al-Ti-B, cast at 325 °C mold temperature.
Both Al-Ti-B grain refiners produced a higher cooling rate in the AZ91D Mg alloy, at both mold temperatures, in comparison to the unrefined alloy. An increase of a cooling rate in grain refined Mg alloys has been reported in literature [8]. This is likely due to a combination of a delayed coherency point and increased rapid heterogenous nucleation of the primary phase producing fine grains, allow heat dissipation to the mold surface via mobile liquid. The addition of Ti, TiB₂, and TiAl₃ substrates to the liquid Mg would provide an increase in heterogenous nucleation throughout the casting [49], [56]. As explained in Section 2.2.1.1.2, heterogenous nucleation lowers the interfacial energy and requires less undercooling to ensure the survival of the forming nuclei. Therefore, the likelihood of more nuclei surviving and growing was increased with grain refinement, thereby accelerating the solidification process. Simultaneously, dissolved Ti was reported to cause growth restriction of the α-Mg phase, as discussed in Section 2.2.2.2.1. Therefore, this could increase the potential for additional nuclei to form and thus further cause grain size reduction.

During the initial stage of solidification for each refined alloy, a similar cooling profile was followed. After cooling from liquidus to below ~525 °C temperature, deviations in the cooling curves were observed. At this instance the fraction of solid reached ~0.8 and the force curves also began to exhibit a large slope change. The shift in the cooling curves was most
likely associated with a change in the dendritic morphology when the liquid Mg formed a significant amount of solid phase.

Considering the force evolution profiles for the grain refined castings, a small force release was observed at ~10-20 seconds into the solidification process. Such a force release may be associated with the nucleation of a hot tear [14], [28]. The force release was more pronounced in the 300 °C mold temperature casting than in the 325 °C mold temperature casting. In the unrefined castings, the force release occurred at ~535 °C, while in the Al-Ti-B refined castings the force release occurred later at ~515 °C. This result suggests that despite the evolving stress on the dendritic structure, the hot tears that may have nucleated were most likely backfilled with mobile eutectic liquid, which would heal them and prevent their further propagation [7], [24] (refer to Appendix D for dendritic structure within grains of as-cast AZ91D).

In the Al-Ti-B refined castings, the fraction of solid when the dendritic structure experienced tensile force was higher than in the unrefined castings, suggesting a delayed tensile coherency point. The tensile coherency fraction of solid for the Al-5Ti-1B and Al-15Ti-3B refined castings at 325 °C was ~0.8 while at 300 °C the fraction of solid was ~0.73. Both of the values were higher than in the unrefined AZ91D Mg alloy, where the tensile coherency fraction of solid was ~ 0.6 to 0.65. The higher fraction of solid at tensile coherency would directly relate to the hot tearing resistance of the Al-Ti-B grain refined castings [9], [19], [75].

Table 4-6 shows that in all AZ91D Mg alloys refined with Al-Ti-B, the force was lower than the force experienced by the unrefined AZ91D Mg alloy. This result suggests that despite the increased cooling rate, a lower overall force developed in the refined castings during solidification. Additionally, in the case of the AZ91D Mg alloy refined with Al-Ti-B, the duration of solidification at the high force levels was shorter than in the case of the unrefined casting. For example, in the AZ91D Mg alloy cast at a 325 °C mold temperature, the Al-5Ti-1B refined alloy showed ~50 sec of solidification time remaining after the inflection, while the
unrefined alloy showed ~91 sec remaining after the inflection. Consequently, the unrefined alloy sustained relatively higher loads for a longer period of time during the solidification period when interdendritic feeding was difficult. As previously observed (Section 4.4.1.1), hot tears readily nucleated and propagated in the unrefined AZ91D Mg alloy.

Selected cooling and load data from castings with the commercial Al-5Ti-1B grain refiner, the SPS Al-5Ti-1B grain refiner, and the unrefined AZ91D Mg alloy castings are provided in Tables 4-7 and 4-8, and Figure 4-98.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Total Solidification Time (s)</th>
<th>Average Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>105.5</td>
<td>1.5</td>
</tr>
<tr>
<td>325</td>
<td>SPS Al-5Ti-1B</td>
<td>68.5</td>
<td>2.3</td>
</tr>
<tr>
<td>325</td>
<td>Commercial Al-5Ti-1B</td>
<td>91.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 4-8: Force Data for AZ91D Mg Alloy Refined with Commercial Al-Ti-B.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Force at Inflection (N)</th>
<th>Force at FS=1 (N)</th>
<th>Solidification Time after Inflection (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>30</td>
<td>70.1</td>
<td>91.5</td>
</tr>
<tr>
<td>325</td>
<td>SPS Al-5Ti-1B</td>
<td>35.4</td>
<td>61.7</td>
<td>50.5</td>
</tr>
<tr>
<td>325</td>
<td>Commercial Al-5Ti-1B</td>
<td>28.1</td>
<td>81.2</td>
<td>81.5</td>
</tr>
</tbody>
</table>

Figure 4-98: (a) Cooling, (b) Force, and (c) Fraction of solid v. Force curves for AZ91D Mg alloy refined with SPS and commercial Al-5Ti-1B, cast at 325 °C mold temperature.
In the case of the commercial Al-Ti-B refiner, the cooling rate only marginally increased from 1.5 °C/s to 1.7 °C/s. In the case of the SPS Al-Ti-B refiner the cooling rate was ~2.3 °C/s. This trend could be correlated to the grain size observations (Section 4.2.4.1) where the SPS Al-5Ti-1B grain refiner produced a significantly lower grain size, while the commercial Al-Ti-B produced only a marginal grain size reduction. Based on the cooling curves, the solidification of the alloy treated with the commercial Al-5Ti-1B refiner followed closely to the solidification of the unrefined casting.

At ~25 seconds, the commercial refined casting showed multiple force relaxations, which suggest hot tear nucleation or propagation, which is consistent with the observed hot tears in the commercial Al-5Ti-1B refined casting.

The commercial Al-5Ti-1B refined casting and the unrefined casting also show similarities in the fraction of solid versus force evolution profile. An appreciable level of force developed at a fraction of solid of ~0.6, at which point the microstructure would not have been solid enough to support the evolving load, and thus hot tears would nucleate to alleviate the solidification stress and strain.

Overall, the commercial Al-5Ti-1B refined casting experienced a similar solidification performance and hot tear susceptibility to the unrefined casting.

### 4.4.2.2 Force and Cooling Curves for Al-Ti-C Grain Refined AZ91D Mg Alloy

The *in-situ* data collected during solidification of the Al-Ti-C refined AZ91D Mg alloy castings are provided in Figure 4-99 and 4-100, and in Table 4-9 and 4-10. Both grain refiners (Al-5.4Ti-0.6 and Al-16.2Ti-1.8C) exhibited nearly identical effect on the AZ91D Mg alloy.

Table 4-9 shows the local solidification time and cooling rate for the grain refined alloys. The results suggest that in the case of the Al-Ti-C grain refiners, an increase in grain refiner concentration increased the cooling rate of the casting. A potential mechanism for this was the effective rapid heterogenous nucleation, as was also observed for the Al-Ti-B refiners.
Table 4-9: Temperature Data for AZ91D Mg Alloy Refined with Al-Ti-C.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Total Solidification Time (s)</th>
<th>Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
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<td>Unrefined</td>
<td>105.5</td>
<td>1.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-5.4Ti-0.6C</td>
<td>86</td>
<td>1.8</td>
</tr>
<tr>
<td>325</td>
<td>Al-16.2Ti-1.8C</td>
<td>75</td>
<td>2.1</td>
</tr>
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<td>Unrefined</td>
<td>48.5</td>
<td>3.2</td>
</tr>
<tr>
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<td>Al-5.4Ti-0.6C</td>
<td>50</td>
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</tr>
<tr>
<td>300</td>
<td>Al-16.2Ti-1.8C</td>
<td>45.5</td>
<td>3.4</td>
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</table>

Table 4-10: Force Data for AZ91D Mg Alloy Refined with Al-Ti-C.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Force at Inflection (N)</th>
<th>Force at FS=1 (N)</th>
<th>Solidification Time after Inflection (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
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<td>70.1</td>
<td>91.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-5.4Ti-0.6C</td>
<td>34.6</td>
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<tr>
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<td>Al-16.2Ti-1.8C</td>
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<td>62.8</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>Unrefined</td>
<td>55.4</td>
<td>77.5</td>
<td>36.5</td>
</tr>
<tr>
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<td>Al-5.4Ti-0.6C</td>
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<td>Al-16.2Ti-1.8C</td>
<td>59.2</td>
<td>77.4</td>
<td>29.5</td>
</tr>
</tbody>
</table>

Figure 4-99: (a) Cooling, (b) Force, and (c) Fraction of solid v. Force curves for AZ91D Mg alloy refined with Al-Ti-C, cast at 325 °C mold temperature.
The variations in the cooling rate during solidification can be observed in the cooling curves in Figure 4-99a and 4-100a. The cooling rate of the Al-Ti-C refined castings follows the same path as the unrefined castings until ~525 °C, at which point the formation of the solid phase initiated.

Figures 4-99b and 4-100b show the force evolution for both grain refiners. In the Al-Ti-C refined castings, at both mold temperatures, a small force release was observed during the initial stages of solidification. This was likely associated with the nucleation of a porosity or a micro hot tear during solidification.

Figure 4-99c and 4-100c show the force evolution as a function of fraction of solid. For the castings made at the 325 °C mold temperature, the fraction of solid when force began to evolve was ~0.7 for both Al-Ti-C refiners. For the castings made at 300 °C mold temperature, the fraction of solid decreased to ~0.6-0.65. As previously discussed, a tensile coherency fraction of solid of ~0.8 or greater is correlated with the elimination of hot tearing in this research (Section 4.4.2.2.1 and 4.4.2.1). Thus, the fraction of solid results observed for the AZ91D Mg alloy refined with Al-Ti-C, agree well with the results of optical microscopy (Section 4.4.1.2.2), where hairline hot tears were observed.
4.4.2.2.3 Force and Cooling Curves for Al-C Grain Refined AZ91D Mg Alloy

Figures 4-101 and 4-102 show the force and cooling curves for the AZ91D Mg alloy treated with the Al-2C and Al-10C refiners. The cooling and force data extracted from the *in-situ* data can be seen in Table 4-11 and 4-12.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Total Solidification Time (s)</th>
<th>Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>105.5</td>
<td>1.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-2C</td>
<td>61.5</td>
<td>2.6</td>
</tr>
<tr>
<td>325</td>
<td>Al-10C</td>
<td>73</td>
<td>2.4</td>
</tr>
<tr>
<td>300</td>
<td>Unrefined</td>
<td>48.5</td>
<td>3.2</td>
</tr>
<tr>
<td>300</td>
<td>Al-2C</td>
<td>46</td>
<td>3.4</td>
</tr>
<tr>
<td>300</td>
<td>Al-10C</td>
<td>45</td>
<td>3.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Force at Inflection (N)</th>
<th>Force at FS=1 (N)</th>
<th>Solidification Time after Inflection (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>30</td>
<td>70.1</td>
<td>91.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-2C</td>
<td>25</td>
<td>52.8</td>
<td>46.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-10C</td>
<td>23.3</td>
<td>64.9</td>
<td>73</td>
</tr>
<tr>
<td>300</td>
<td>Unrefined</td>
<td>55.4</td>
<td>77.5</td>
<td>36.5</td>
</tr>
<tr>
<td>300</td>
<td>Al-2C</td>
<td>38.7</td>
<td>63.1</td>
<td>30</td>
</tr>
<tr>
<td>300</td>
<td>Al-10C</td>
<td>41</td>
<td>59.9</td>
<td>25.5</td>
</tr>
</tbody>
</table>
As previously observed with the Al-Ti-B and Al-Ti-C refiners, the Al-C grain refiner also resulted in an increase of the cooling rate. Since each of the grain refiners were compositionally different, the results suggest that the primary grain refining mechanism was related to rapid heterogeneous nucleation. This likely resulted in increased grain surface area during solidification, allowing increased heat dissipation, and therefore, higher cooling rates as observed by the cooling curves in Figure 4-101a. This result has been observed in literature where grain refinement was analyzed in permanent mold castings in AZ91E Mg alloy [8].
As seen in Table 4-11, the faster cooling for the Al-C refined castings was only observed at the 325 °C mold temperature, whereas at the 300 °C mold temperature, for both Al-C refined AZ91D Mg alloy, the cooling rate was only slightly higher than the unrefined casting. Figures 4-101a and 4-102a show the temperature profile during solidification of the AZ91D Mg alloy treated with the Al-2C and Al-10C refiners. For all castings (similar to other refiners discussed previously), each cooling curve follows the same general trend of a sharp initial slope which changed at ~525 °C, when the refined castings show divergence from the unrefined casting’s cooling rate. This effect was also observed with the previously discussed refiners.

In the force curves for the Al-2C and Al-10C refined AZ91D Mg alloy cast at 325 °C mold temperature, a small force relaxation was observed before the inflection point. This may have been a hot tear nucleating; however, microstructure analysis (Section 4.4.1.2.3) suggests that such nucleated hot tears would have been healed by interdendritic liquid, since no hot tears were visible in the casting. In the case of the force curves for the 300 °C mold temperature castings, a similar relaxation in the force curve was observed, but here the interdendritic liquid was not able to accommodate the solidification shrinkage, and hot tears remained in the casting, as observed in Section 4.2.4.3.

Figures 4-101c and 4-102c show the fraction of solid compared to the force evolution during solidification for the Al-2C and Al-10C refined AZ91D Mg alloys. A tensile coherency fraction of solid of ~0.75 was observed at both mold temperatures of the Al-2C and Al-10C refined AZ91D Mg alloys. As previously discussed (Section 4.4.2.1, 4.4.2.2.1, 4.4.2.2.2), the increased tensile coherency fraction of solid was likely a contributing factor to the increased hot tear resistance.

Table 4-12 shows that the Al-2C and Al-10C grain refined alloys consistently showed a lower force at the inflection, irrespective of the mold temperature. This trend has not been observed with other refiners. This result suggests that a lower force developed during the
final stages of solidification, likely leading to a decreased hot tearing severity. Also, the force at the end of solidification was reduced by ~20N due to the Al-2C refiner at both mold temperatures. With the Al-10C refiner, the force at the end of solidification was reduced by ~10N at 325 °C and ~20N at 300 °C mold temperatures, respectively. Therefore, the refined microstructure of the Al-C refined alloys was likely able to better distribute and accommodate the contraction force caused by shrinkage leading to an improvement in hot tearing resistance.

4.4.2.2.4 Force and Cooling Curves for Al-Ti Grain Refined AZ91D Mg Alloy

Tables 4-13 and 4-14 show the cooling and force data for the Al-Ti refined castings, while Figures 4-103 and 4-104 show the cooling and force curves for the 325 °C and 300 °C mold temperature casting, respectively.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Total Solidification Time (s)</th>
<th>Cooling Rate (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>105.5</td>
<td>1.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-6Ti</td>
<td>61</td>
<td>2.6</td>
</tr>
<tr>
<td>325</td>
<td>Al-18Ti</td>
<td>66</td>
<td>2.4</td>
</tr>
<tr>
<td>300</td>
<td>Unrefined</td>
<td>48.5</td>
<td>3.2</td>
</tr>
<tr>
<td>300</td>
<td>Al-6Ti</td>
<td>36</td>
<td>4.35</td>
</tr>
<tr>
<td>300</td>
<td>Al-18Ti</td>
<td>35.5</td>
<td>4.45</td>
</tr>
</tbody>
</table>
Table 4-14: Force Data for AZ91D Mg Alloy Refined with Al-Ti.

<table>
<thead>
<tr>
<th>Mold Temperature (°C)</th>
<th>Refiner</th>
<th>Force at Inflection (N)</th>
<th>Force at FS=1 (N)</th>
<th>Solidification Time after Inflection (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>Unrefined</td>
<td>30</td>
<td>70.1</td>
<td>91.5</td>
</tr>
<tr>
<td>325</td>
<td>Al-6Ti</td>
<td>28.2</td>
<td>54.1</td>
<td>51</td>
</tr>
<tr>
<td>325</td>
<td>Al-18Ti</td>
<td>24.1</td>
<td>56.1</td>
<td>54.5</td>
</tr>
<tr>
<td>300</td>
<td>Unrefined</td>
<td>55.4</td>
<td>77.5</td>
<td>36.5</td>
</tr>
<tr>
<td>300</td>
<td>Al-6Ti</td>
<td>33.2</td>
<td>50.3</td>
<td>25.5</td>
</tr>
<tr>
<td>300</td>
<td>Al-18Ti</td>
<td>49.9</td>
<td>56.2</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure 4-103: (a) Cooling, (b) Force, and (c) Fraction of solid v. Force curves for AZ91D Mg alloy refined with Al-Ti, cast at 325 °C mold temperature.

Figure 4-104: (a) Cooling, (b) Force, and (c) Fraction of solid v. Force curves for AZ91D Mg alloy refined with Al-Ti, cast at 300 °C mold temperature.

From the cooling rate data, both Al-Ti grain refiners have increased the cooling rate by ~1°C/s with respect to the unrefined AZ91D Mg alloy. At the end of solidification in the
unrefined AZ91D Mg alloy, a force of ~70 N and ~80 N had evolved for the 325 °C and 300 °C mold temperatures, respectively. In the Al-6Ti and Al-18Ti refined AZ91D Mg alloys, the force at the end of solidification was lower at ~55 N.

Both Al-Ti refiners treated produced similar cooling curves, suggesting that an increase in Ti content did not alter the cooling kinetics. Similarly, as with other refiners previously discussed, the divergence between the unrefined and the refined alloys began at ~525 °C. As suggested previously, heterogenous nucleation most likely caused the increase in the cooling rate.

The force curves for the Al-Ti refined alloy are provided in Figure 4-103b and 4-104b. In all castings, the large inflection recorded in the force curves was at ~15 seconds into solidification. The fraction of solid at this point was >~0.8 and therefore more time spent solidifying after stage will likely increased the tendency of hot tearing [9], [22], [27] since liquid feeding would be highly impeded [14], [27], [53]. For the Al-Ti refined AZ91D Mg alloy, a reduced load during this stage was observed along with a shorter time period of remaining solidification in comparison to the unrefined AZ91D Mg alloy, leading to a decrease in hot tear susceptibility.

In Figure 4-103c and 4-104c, the fraction of solid based on the in-situ cooling data is plotted against the force evolution. The AZ91D Mg alloy refined with the Al-6Ti and Al-18Ti, which had ~76% reduction in grain size (Section 4.2.4.4), show a tensile coherency fraction of solid of ~0.8. The higher tensile coherency fraction of solid, close to and greater than ~0.8, has been consistently observed in castings where hot tearing was reduced and/or eliminated (Sections 4.4.2.1, 4.4.2.2.1, and 4.4.2.2.3).
Chapter 5: Conclusion

The fundamental scientific contribution of this thesis was to the area of grain refinement of Al-bearing Mg alloys. Using spark plasma sintering, several novel grain refiners were fabricated and observed to provide a significant grain refinement of the AZ91D Mg alloy. Some of the additional benefits included improved mechanical properties, improved secondary phase distribution, leading to the reduction of hot tear casting defects. Further, new insights were gained by using a novel instrumented constrained-rod casting mold. Most notably, the application of neutron diffraction to study the solidification of unrefined and refined AZ91D Mg alloy revealed the effect of refinement on the solidification of the alloy. It was found that refinement caused a delayed evolution of the primary phase and an accelerated evolution of the secondary phase. This has been attributed to finer grains during solidification, improved feeding capabilities within the alloy and a change in the secondary phase morphology. These findings provide designers and modellers a better understanding of the impact grain refinement has on the solidification of Mg alloys.

The specific conclusions of each Section are listed as follows:

5.1 AZ91D Mg Alloy

1. Successful analysis of AZ91D Mg alloy using a force contraction mold was completed. The in-situ temperature and force data provided insight into force events related to the nucleation and propagation of hot tears during solidification. Additionally, as seen in literature, the hot tearing severity increased proportionally to the cooling rate which was controlled via the mold temperature.

2. Hot tearing was eliminated in the AZ91D Mg alloy when cast at a mold temperature of 350 °C; the cooling rate in the casting was ~1 °C/s. Additionally, in the unrefined alloy the tensile coherency fraction of solid required to effectively resist hot tearing was found to be ~0.82.
5.2 Spark Plasma Sintered Grain Refiners

1. Spark Plasma Sintering was a successful method to produce the Al-Ti-B, Al-Ti-C, Al-C, and Al-Ti grain refiners. The efficiency of the SPS process allowed 8 different grain refiners to be produced.

2. The effectiveness of the SPS’ed refiners was attributed to a good particle distribution and enhanced wetting due to the formation of an Al intermediate layer around refining particles, leading to improved heterogenous nucleation of α-Mg during the solidification.

3. A commercially available Al-5Ti-1B grain refiner was successfully compared to the SPS’ed Al-5Ti-1B refiner. The SPS’ed refiner was found to have outperformed the commercial refiner due to the presence of the Al intermediate layer and better particle distribution. Significantly, spectrum and XRD analysis revealed that the composition in the commercial refiner was lower than advertised which would likely decreased the performance.

5.3 Microstructural Analysis of Grain Refined AZ91D Mg Alloy

1. Effective grain refinement was observed with each SPS’ed refiner manufactured, suggesting the powder metallurgical process is an effective method to produce grain refiners for AZ91D Mg alloy.

2. The most effective grain refiner was found to be the Al-18Ti refiner, which produced a grain size reduction of ~80% in the AZ91D Mg alloy. The Al-18Ti grain refiner produced a homogenous microstructure throughout the casting and a good distribution of the secondary phases.

3. The commercially available Al-5Ti-1B refiner did not provide the same level of grain refinement as the SPS Al-5Ti-1B refiner. The grain size reduction in the AZ91D Mg
alloy due to the SPS’ed refiner was an additional ~25-30% compared to the commercial refiner. Additionally, greater microstructure homogeneity was found in the alloy treated with the SPS’ed refiner.

5.4 Diffraction Analysis of Grain Refined AZ91D Mg Alloy

1. Electron Back Scattered Diffraction (EBSD) was successfully completed on as-cast AZ91D Mg alloy. Only a slight non-uniform distribution was observed in the unrefined alloy while a more random distribution was observed in the SPS’ed grain refined alloy.

2. The solidification process of the unrefined and refined AZ91D Mg alloys was successfully captured with in-situ Neutron Diffraction analysis. The diffraction peaks that represent the alloy were collected at 24 temperatures points ranging from 635 °C to 40 °C.

3. In-situ Neutron Diffraction solidification analysis of the Al-Ti-C and Al-C refined AZ91D Mg alloys showed the fraction of solid evolution was consistently lower than the unrefined alloy. Furthermore, during the late stages of solidification (>~0.8 fraction of solid), the refined alloys maintained more liquid phase until the complete solid was reached.

4. Successful detection of the low volume fraction β-Mg₁₇Al₁₂ phase during solidification was completed with Neutron Diffraction. The refined AZ91D Mg alloys showed a rapid evolution of the β-Mg₁₇Al₁₂ phase immediately after solidification of the primary phase was complete.

5. Using the Rietveld refinement technique, quantification via weight percent of α-Mg and β-Mg₁₇Al₁₂ phases present during and after solidification was completed. A reduced quantity of β phase and an inversely proportional increased quantity of α-Mg phase was observed in the refined alloys, which was consistent with XEDS data of
the unrefined and refined alloys. This was attributed to the grain refiners causing decreased diffusion of Al out of the α-Mg phase (i.e., less Al available for β phase).

5.5 Hot Tearing Analysis of Grain Refined AZ91D Mg Alloy

1. The most effective grain refiner for the reduction of hot tearing was the Al-18Ti refiner as it had removed hot tearing at both mold temperatures. This was consistent with the excellent microstructural refinement observed by this refiner.

2. The AZ91D Mg alloy treated with many of the SPS’ed grain refiners consistently showed an increased cooling rate. On average, for castings at the 325 °C mold temperature, the cooling rate increased by ~60%, while at the 300 °C mold temperature the cooling rate increased by ~30%. This was attributed to rapid heterogenous nucleation causing an increased density of finer grains in the liquid, collectively increasing the solid surface area to dissipate latent heat to the casting mold.

3. The force and temperature data that were collected during solidification was successfully correlated via the fraction of solid. Comparison of the fraction of solid and force evolution has provided new insight on the solidification process.

4. Comparing the unrefined and refined AZ91D Mg alloy castings, a higher fraction of solid, when load developed, was detected in the refined castings. This was likely the dominant factor for the increased hot tearing resistance produced by many of the SPS’ed refiners in the AZ91D Mg alloy.
5.6 Future Work

The results of this research have opened many paths for future research. As well, industrial implementation of this research is likely to occur given the effectiveness of the novel refinement. Some of the future work related to this research includes:

1. *In-situ* solidification analysis of light alloys: a hot tearing study

   This research would involve the application of an *in-situ* solidification analysis method such as neutron diffraction or synchrotron light source, to study hot tearing in a force contraction mold.

2. *In-situ* solidification analysis of grain refined Mg-Al alloys

   This study, similar to the previous, would use various *in-situ* solidification analysis methods to study the exact grain refinement mechanism occurring in Al-bearing Mg alloys, specifically with carbon refinement. Further understanding of the carbon refinement mechanism would likely allow casting designers better tools to optimize grain refinement of Al-bearing Mg alloys.

3. Manufacturing of spark plasma sintered grain refiners

   This research would involve selecting one of the previously mentioned refiners and studying the sintering process. As well, further analysis into the intermediate boundary layer present at the particle interface and quantification of the kinetics of formation of the intermediate layer. Additionally, analysis of various ratios of refining particles to Al matrix, to find the optimal ratio to produce the largest nucleation potential in Al and Mg alloys, while still being economically viable to industry.
Bibliography


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2017.


[104] D. Sediako and W. Kasprzak, “In Situ Study of Microstructure Evolution in


Appendices

Appendix A: In-situ Data Collected

This Section discusses the preliminary in-situ force and temperature data collected during the hot tearing experiments. Additionally, the repeatability of the experimental setup is shown.

A.1 Repeatability of Hot Tearing Setup

The repeatability of the hot tearing setup was previously validated in literature but was ensured in this research. Figure A-1 shows the repeatability results for unrefined AZ91D Mg alloy cast in the hot tear mold.

![Figure A-1: Repeatability of cooling and force curves for unrefined AZ91D Mg alloy cast at 350 °C mold temperatures.](image)
A.2 Initial Casting Trials

Initial casting trials were completed at mold temperatures starting at 200 °C, incrementally increased by 25 °C, as previously stated in the experimental procedure. Figure A-2 shows the cooling and force curves for experiments completed at mold temperatures from 200 °C to 275 °C.

Figure A-2: Cooling and force curves for unrefined AZ91D Mg alloy cast at various mold temperatures.
Appendix B: Macro Images of Surface in Critical Hot Tear Region

Images of the surface in the critical hot tear region were collected for each casting. This showed the superficial evidence of the hot tearing severity, giving a preliminary comparison.

B.1 Unrefined Castings

Figure B-1: Macro images of the surface at the critical hot tear region for the unrefined AZ91D Mg alloy, cast at 350 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-2: Macro images of the surface at the critical hot tear region for the unrefined AZ91D Mg alloy, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.
Figure B-3: Macro images of the surface at the critical hot tear region for the unrefined AZ91D Mg alloy, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

A.2 Refined Castings

Figure B-4: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-5Ti-1B, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-5: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-15Ti-3B, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.
Figure B-6: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with commercial Al-5Ti-1B, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-7: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-5Ti-1B, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-8: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-15Ti-3B, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.
Figure B-9: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-5.4Ti-0.6C, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-10: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-16.2Ti-1.8C, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-11: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-5.4Ti-0.6C, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.
Figure B-12: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-16.2Ti-1.8C, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-13: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-2C, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-14: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-10C, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.
Figure B-15: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-2C, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-16: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-10C, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-17: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-6Ti, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.
Figure B-18: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-18Ti, cast at 325 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-19: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-6Ti, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.

Figure B-20: Macro images of the surface at the critical hot tear region for the AZ91D Mg alloy refined with Al-18Ti, cast at 300 °C mold temperature; (a) Top, (b) Bottom, (c) Right Side, and (d) Left Side.
Appendix C: Analysis of Neutron Diffraction Data

Explanation of the exact correction method will be discussed with a full calculation example shown. Additionally, the methodology to the Rietveld and MAUD software application will be explained.

C.1 Fraction of solid Calculations

For the sample calculation of the fraction of solid from the neutron diffraction solidification data, the \{0002\} peak/reflection from the unrefined AZ91D Mg alloy will be used.

The first step was to isolate the peak from the diffraction pattern for each temperature step. The result is shown in Figure C-1. Depending on the peak size and its position relative to other peaks, ~2° on either side of the peak would be included when isolating the peak. This was required for calculating the background intensity.

![Figure C-1: \{0002\} peak for the α-Mg phase, isolated from the neutron solidification data of the unrefined AZ91D Mg alloy.](image)

Once the peak was isolated, the area under the peak could be found for each temperature step. It was found that 9 data points, 4 on either side of the highest count point, was sufficient for finding the total peak area. As the temperature decreased, the peak location
shifted to the right and so the 9 data points across the peak were found at each temperature step. Finally, the sum of the 9 data points that made up the peak, gave the peak area with background; the area was calculated at each temperature. Figure C-2 shows the first few temperature points where the peak area with background.

<table>
<thead>
<tr>
<th>SUM of Data Points</th>
<th>46380</th>
<th>43004</th>
<th>41037</th>
<th>37317</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUM of Peak w/ BG</td>
<td>13580</td>
<td>12999</td>
<td>14315</td>
<td>13932</td>
</tr>
<tr>
<td>BG</td>
<td>1490.91</td>
<td>1363.86</td>
<td>1214.636</td>
<td>1062.955</td>
</tr>
<tr>
<td>Peak w/o BG</td>
<td>161.818</td>
<td>724.227</td>
<td>3383.273</td>
<td>4365.409</td>
</tr>
<tr>
<td>FS %</td>
<td>0</td>
<td>0.02879</td>
<td>0.164922</td>
<td>0.215202</td>
</tr>
</tbody>
</table>

Figure C-2: Initial peak data leading to the fraction of solid for 630 to 575 °C for the {0002} peak for the α-Mg phase, isolated from the neutron solidification data of the unrefined AZ91D Mg alloy.

The next step was to find the peak area without background. All points, excluding the 9 data points for the peak, were summed, then averaged to find the average background for the specific temperature step. The background intensity was found to decrease as the temperature decreased. The peak area without background was then found by subtracting the sum of the background across the 9 data points, from the peak area with background, previously found. Again, this process was completed for each temperature step. The final peak area without background is shown in Figure C-2.

The initial fraction of solid at each temperature step could be found by making a relative comparison of the peak area without background. To do this, the liquidus and solidus points had to be determined. The liquidus temperature used was based on the theoretical value of the alloy. The solidus value was found based on when the peak intensity first showed signs of repeating. In this work, the solidus temperature was found to be consistent with the theoretical solidus of the AZ91D Mg alloy. A relative fraction of solid at each temperature
could be found using the peak area without background at the temperature step closest to the solidus. In some cases, the solidus may have occurred at a temperature where no diffraction data was collected. Figure C-3 shows the initial fraction of solid curve based on the above calculations.

![Image](image.jpg)

**Figure C-3**: Initial fraction of solid curve for the \{0002\} peak for the \(\alpha\)-Mg phase, isolated from the neutron solidification data of the unrefined AZ91D Mg alloy.

The final step was to correct the fraction of solid curve for the Debye-Waller (DW) effect.

First, the fraction of solid values for temperatures past the solidus (i.e., greater than 1) were plotted. This can be seen in Figure C-4.
Figure C-4: Production of the Debye-Waller correction factor to be applied to the fraction of solid curve for the (0002) peak for the α-Mg phase, isolated from the neutron solidification data of the unrefined AZ91D Mg alloy.

A trendline was then found for the points and the equation for the trendline was produced. The equation was then used (the “x” value was replaced) with the temperature and the corresponding initial fraction of solid value was multiplied to find the correction factor for that specific temperature step. The correction factor would then be subtracted from the corresponding fraction of solid value to produce a “corrected” fraction of solid value. This was repeated for each temperature and corresponding fraction of solid value. Figure C-5 shows the results of the correction factor application.
Figure C-5: First application of the Debye-Waller correction factor to the initial fraction of solid curve for the \{0002\} peak for the \(\alpha\)-Mg phase, isolated from the neutron solidification data of the unrefined AZ91D Mg alloy.

This process of correcting the fraction of solid value for each temperature was completed until no significant changes between the corrected and uncorrected are observed. The final fraction of solid curve is shown in Figure C-6.

Figure C-6: Final application of the Debye-Waller correction factor to the fraction of solid curve for the \{0002\} peak for the \(\alpha\)-Mg phase, isolated from the neutron solidification data of the unrefined AZ91D Mg alloy.
C.2 MAUD Software for Rietveld Refinement

MAUD software was used to perform the Rietveld refinement technique of the neutron diffraction data collected during solidification, to determine the weight percent of detected phases. Figure C-7 and C-8 shows the plot and results produced from the MAUD software. Figure C-8 shows the final weight percent of each phase present in the pattern shown in Figure C-7. The Rietveld refinement technique was repeated twice for each pattern analyzed in the MAUD software.

Figure C-7: MAUD plot produced from the 40 °C temperature step of the neutron diffraction solidification data of the unrefined AZ91D Mg alloy.
C.3 Fraction of Solid Comparison

As discussed in Section 3.6.2 of the experimental procedure, the fraction of solid model developed by Tacke et. al. [107] correlated well with the experimental fraction of solid curves produce via neutron diffraction. Figure C-9 shows the results of the comparison.
Figure C-9: Comparison of experimental and mathematical fraction of solid model for AZ91D Mg alloy.
Appendix D: Dendritic Structure of as-cast AZ91D Mg Alloy

Figure D-1 to D-3 act as representative micrographs of the dendritic structure within the grains of the as-cast AZ91D Mg alloy.
Figure D-1: Dendritic structure in the as-cast AZ91D Mg alloy.
Appendix E: Differential Scanning Calorimetry (DSC) Data

Preliminary DSC analysis was completed on some of the refined castings. The results indicated the liquidus and solidus, which was consistent with literature. Figure E-1 shows the DSC curves for unrefined, Al-15Ti-3B refined, Al-16.2Ti-1.8B refined, and Al-10C refined AZ91D Mg alloy.

Figure E-1: DSC curves for unrefined, Al-15Ti-3B refined, Al-16.2Ti-1.8B refined, and Al-10C refined AZ91D Mg alloy.