SEMI-SOLID SLURRY FORMATION VIA LIQUID METAL MIXING

A Thesis

Submitted to the Faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the

Degree of Master of Science

in

Materials Science and Engineering

July 2003

by

Matthew M. Findon

APPROVED:

______________________________
Diran Apelian, Howmet Professor of Engineering, Advisor

______________________________
Richard D. Sisson, Jr., Professor of Mechanical Engineering, Materials Science and Engineering Program Head
Abstract

New, economical semi-solid metal (SSM) processes rely on forced convection during solidification to influence non-dendritic growth. The fundamental mechanisms that produce SSM microstructures in the presence of forced convection (due to fluid flow) are not fully understood. The objective of this work is to elucidate these mechanisms through the use of a new semi-solid slurry-making technique. Employing an apparatus developed at WPI, two alloy melts are mixed within a static reactor that induces convection and rapid cooling. Experiments carried out with this apparatus, named the “Continuous Rheoconversion Process” (CRP), result in globular semi-solid microstructures throughout a wide range of processing conditions. These conditions include the superheat in the melts before mixing, cooling rate of the slurry through the SSM range, and the presence or absence of inoculants in the melts.

The results comprise repeatable sets of semi-solid microstructures having fine particle size and shape factors approaching unity. Even in the absence of melt inoculants, uniform distributions of $\alpha$-Al particle sizes of about 60$\mu$m are attainable. Entrapped liquid is not present in the majority of the samples obtained with the CRP, and irregular particles that form in the process are of a limited distribution. Variation of slurry analysis methods indicates that these structures can be obtained consistently for both thixocasting and rheocasting applications.

The design of the mixing reactor leads to turbulent fluid flow just as solidification commences. The results suggest that the following factors must be considered in identifying the mechanisms operating under the above conditions: copious nucleation of the primary phase; dispersion of nuclei throughout the bulk liquid; and
inhibited remelting of nuclei due to temperature uniformity. In the CRP, these factors consistently lead to suppression of dendritic growth, significant grain refinement, and globular slurries. The exact fundamental mechanism leading to this effect is yet to be uncovered; however it is clear that temperature gradients ahead of the liquid are such that a cellular, non-dendritic morphology is the most stable growth form. Through further exploration of the process and identification of the operating mechanisms, future development of economical, continuous rheocasting methods will be facilitated.
Acknowledgements

First and foremost, I would like to express my gratitude to my thesis advisor, Prof. Diran Apelian, for his immense support throughout this project, both scientifically and personally. His wisdom and guidance affected me in such a way as to effect my full potential as a graduate student here at MPI.

I would also like to thank the entire faculty and staff of MPI for their scientific support and overall comradery. I especially thank Dr. Riddle for helping to improve my metallography skills, as well as Dr. Shankar for his helpful instruction concerning image analysis. Carl Raatikainen was quite helpful with apparatus modifications, and without him I may have forgotten about all the things that mysteriously got broken in my presence.

Nick Saddock and Dr. Anacleto de Figuere do deserve mention for the roles they played in the design and construction of the apparatus used for this work. I also appreciate the help from Todd Billings and Steve Derosier in Washburn Shops in making modifications to apparatus components, and I thank Joe Brooks for machining the reactors.

Finally, I would like to thank Prof. Apelian, Prof. Makhlouf, Prof. Sisson, Dr. Pan, and Dr. Shankar for being on my thesis committee and considering this work for the completion of my Master of Science degree.
CONTENTS

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

Acknowledgements .............................................................................................................................. iv

List of Figures and Tables .................................................................................................................... vii

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

2. Background ....................................................................................................................................... 4
   2.1. History of semi-solid metal processing ...................................................................................... 4
   2.2. Previously proposed mechanisms for SSM structure formation ................................................. 23

3. Research Approach ........................................................................................................................... 26

4. Experimental Methodology ............................................................................................................. 28
   4.1. The Continuous Rheoconversion Process (CRP) ........................................................................ 28
      4.1.1. The Apparatus ...................................................................................................................... 28
      4.1.2. Process Variables ............................................................................................................... 37
   4.2. Experimental Plan ....................................................................................................................... 38
      4.2.1. Preliminary work .................................................................................................................. 39
      4.2.2. Alloys used .......................................................................................................................... 39
      4.2.3. Slurry collection method .................................................................................................... 41
      4.2.4. Thixocasting experiments: Variable thermal conditions ....................................................... 43
      4.2.5. Rheocasting experiments: Immediately quenched slurry .................................................... 45
      4.2.6. Rheocasting experiments: Various slurry collection temperatures ..................................... 45
      4.2.7. Rheocasting experiments: Single slurry collection temperature ......................................... 46
   4.3. Experimental Procedures ............................................................................................................. 47
5. **Results and Discussion** ................................................................. 50

5.1. Thixocasting route ................................................................. 50

5.1.1. Variable: Superheat .......................................................... 50

5.1.2. Variable: Reactor temperature ............................................ 55

5.2. Rheocasting route ................................................................. 60

5.2.1. Immediately quenched slurry .............................................. 61

5.2.2. Slurry quenched at various SSM temperatures ...................... 63

(a) Slow cooling rate through SSM range ...................................... 65

(b) Higher cooling rate with variable grain refinement .................. 67

5.2.3. Slurry quenched at a single SSM temperature ....................... 73

(a) High cooling rate through SSM range ...................................... 75

(b) One melt vs. two melts ......................................................... 76

5.3. Cooling rate vs. particle size .................................................. 78

5.4. Discussion of potential mechanisms ....................................... 80

6. **Conclusions** ........................................................................ 85

7. **References** .......................................................................... 88

**Appendix A: Micrograph gallery** .............................................. 91

**Appendix B: Control experiments – Liquid metal transport tubes** .... 97
LIST OF FIGURES AND TABLES

Figure 1: Viscosity and shear stress vs. fraction solid of (a) dendritic and (b) non-dendritic Sn-15wt%Pb under a continuous shear rate [5].............5

Figure 2: (a) Dendritic structure (quenched at 0.36 fraction solid) resulting from shearing after solidification begins; (b) Non-dendritic structure (quenched at 0.60 fraction solid) resulting from shearing before solidification begins (Alloy: Sn-15%Pb) [1]........................................6

Figure 3: Hysteresis loop of shear stress vs. shear rate in semi-solid A357 slurry [8]....7

Figure 4: Transmission belt cover produced by an SSM process [3]............................9

Figure 5: Multilink suspension component produced by an SSM process [3]..............9

Figure 6: Schematic of the two major semi-solid processing approaches [2]..............10

Figure 7: SSM structure obtained using the MHD process. Alloy: A356 [2]............12

Figure 8: Structure produced by the Microcast-X (MX) process.
Alloy: MarM247 [2]..........................................................14

Figure 9: General steps involved in UBE’s new rheocasting (NRC) process [2].........15

Figure 10: Typical microstructure obtained with the UBE process.
Alloy: Al-Si-Cu [2]................................................................16

Figure 11: (a) Illustration of the steps involved in the SSR process (b) Typical thermal history of SSR-processed slurry [2] ........................................17

Figure 12: Microstructure of slurry produced using the SSR process.
Alloy: A356 [2]..................................................................18

Figure 13: Time-temperature data from original liquid mixing experiment by Nasim Alem [21].................................................................19

Figure 14: Microstructure obtained from original liquid mixing experiment by Nasim Alem [21].................................................................20

Figure 15: SSM microstructure obtained with the SLC process. Alloy: A356 [25]....21

Figure 16: Sn-15wt%Pb alloy continuously sheared at 3625s⁻¹ in a twin-screw extruder, and quenched at 13°C below its liquidus temperature [27].......24

Figure 17: Early schematic of the Continuous Rheoconversion Process (CRP)........29
Figure 18: Photograph of the CRP apparatus ..........................................................30

Figure 19: (a) Stopper rod and exit spout; (b) a top-down view of the crucible within the melting furnace, showing the pull-action solenoid.................................31

Figure 20: Coiled heating elements used for heating the liquid metal transport tubes...32

Figure 21: “Boot” component of the CRP...............................................................33

Figure 22: Inner designs of the preliminary (left) and secondary (right) mixing reactors.................................................................34

Figure 23: Setup of the third furnace when the reactor is preheated.......................35

Table 1: Chemical compositions (wt%) and liquidus temperatures (°C) of the alloys used.........................................................................................40

Figure 24: Schematic diagrams detailing the solidification paths undergone in the two experimental phases. Arrows indicate quenching of slurry.........................42

Figure 25: Flow chart of the three sample collection methods.................................43

Table 2: Experiments carried out in the “T1” series.............................................44

Table 3: Experiments carried out in the “T2” series.............................................44

Table 4: Experiments carried out in the “R2” series.............................................45

Table 5: Experiments carried out in the “R3” series.............................................47

Table 6: Conditions and thermal results for selected T1 (superheat-variable) experiments.........................................................................................51

Figure 26: (a) As-solidified and (b) reheated microstructures from experiment T1-2. Residence time of reheated slug in SSM range: 38 minutes...............52

Figure 27: (a) As-solidified and (b) reheated microstructures from experiment T1-3. Residence time of reheated slug in SSM range: 25 minutes...............52

Figure 28: (a) As-solidified and (b) reheated microstructures from experiment T1-4. Residence time of reheated slug in SSM range: 18 minutes...............52

Table 7: Image analysis results for the T1 experiments.......................................53

Table 8: Conditions and thermal results for selected T2 (variable reactor temperature) experiments.................................................................56
Figure 29: (a) As-solidified and (b) reheated microstructures from experiment T2-4. Residence time of reheated slug in SSM range: 24 minutes

Figure 30: (a) As-solidified and (b) reheated microstructures from experiment T2-5. Residence time of reheated slug in SSM range: 25 minutes

Figure 31: (a) As-solidified and (b) reheated microstructures from experiment T2-6. Residence time of reheated slug in SSM range: 16 minutes

Figure 32: (a) As-solidified and (b) reheated microstructures from experiment T2-8. Residence time of reheated slug in SSM range: 2 minutes

Table 9: Image analysis results for the T2 experiments

Figure 33: Microstructures from experiment R1-1. The sample was immediately quenched in water upon exit from the reactor

Table 10: Image analysis results for experiment R1-1

Table 11: Conditions and thermal results for the R2 (slurry quenching I) experiments

Figure 34: Microstructural results from experiment R2-2; slurry samples obtained at the specified temperatures and times after slurry collection.

Table 12: Image analysis results for experiment R2-2

Figure 35: Slurries obtained using grain refined A356.2 (above left), SiBloy® (above right), and non-grain refined A356.2 (bottom). Samples quenched at 600°C (1.8min and 2.0min after collection, respectively)

Figure 36: Slurries obtained using grain refined A356.2 (above left), SiBloy® (above right), and non-grain refined A356.2 (bottom). Samples quenched at 590°C (2.3min and 2.8min after collection, respectively)

Figure 37: Slurries obtained using grain refined A356.2 (above left), SiBloy® (above right), and non-grain refined A356.2 (bottom). As-solidified structures

Table 13: Image analysis results for experiments R2-5 through R2-7

Figure 38: R2-5 microstructures at 50X (left) and 200X (right). Sample quenched at 610°C (50 seconds after collection)

Table 14: Image analysis results for the micrographs shown in Figure 38
Table 15: Conditions and thermal results for selected R3 (slurry quenching II) experiments

Figure 39: Microstructures from experiment R3-1; 50X (left), 100X (right)

Figure 40: Microstructures from experiment R3-4; 25X (left), 50X (right)

Figure 41: Microstructures from experiment R3-5; 25X (left), 50X (right)

Table 16: Image analysis results for the R3 experiments

Figure 42: Particle size as a function of cooling rate of the slurry after exiting the reactor. As-solidified structures

Figure 43: Particle size as a function of cooling rate of the slurry after exiting the reactor. Slurry structures at 590°C

Figure 44: Schematic of the solid/liquid interface arising from a single growing equiaxed particle

Figure 45: Schematic of the solid/liquid interfaces arising from multiple growing, closely spaced equiaxed particles

Figure A-1: Experiment R2-2; T_{slurry}=597°C. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth. Note the large size of the dendrite, which likely originated from a small portion of liquid that exited the reactor above its liquidus temperature

Figure A-2: Experiment R2-2; T_{slurry}=590°C. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth

Figure A-3: Experiment R2-2; T_{slurry}=585°C. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth. Unusual dendritic morphologies seen throughout the picture at the right

Figure A-4: Figure A-4: Experiment R2-2; T_{slurry}=605°C. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth

Figure A-5: Experiment R2-2; As-solidified structure. (Left) 25X; (Right) 50X. The presence of the observed eutectic “pool” was not seen in any other samples, but it could be a normal phenomenon due to liquid segregation. “Chinese script” phase observed within the pool is likely the compound Al3Mg3FeSi6, while the black phase seen above this region is probably Mg2Si
Figure A-6: Experiment R3-2; T_{slurry}=585°C. (Left) Non-primary phase particle (possibly β-Si) which seems to be nucleating α-Al; (Right) Quenching artifacts near the thermocouple’s stainless steel protection sheath (far right) ……………………………………………………………………………93

Figure A-7: Experiment R2-2; T_{slurry}=575°C. (Left) 50X, showing several more non-primary phase particles resembling β-Si; (Right) 400X, close-up of acicular Al₅FeSi intermetallic compound……………………………………………………94

Figure A-8: SEM micrographs of the primary Si particles observed in Figure A-7 (top); EDX spectrum of the particle in the right-hand picture, showing only the presence of silicon (bottom) ………………………………………………………………95

Figure A-9: Experiment R2-2. (Left) T_{slurry}=575°C (Right) T_{slurry}=605°C. Well-developed dendrites observed………………………………………………96

Figure A-10: (Left) Experiment R3-4, transition zone between globular and dendritic morphologies; T_{slurry}=585°C (Right) Experiment R3-5, quenching artifacts adjacent to thermocouple’s stainless steel protection sheath; T_{slurry}=585°C…………………………………………………………………………96

Table B-1: Conditions and thermal data for the tube control experiments…………………97

Figure B-1: Microstructure obtained when a hot tube was employed (experiment TC-1). Quenched in water………………………………………………98

Figure B-2: Microstructure obtained when a cold tube was employed (experiment TC-2). Quenched in water………………………………………………98
1. Introduction

Semi-solid metal (SSM) processing is a promising technology that resulted from groundbreaking findings in the early 1970’s at the Massachusetts Institute of Technology [1]. Since the initial discovery, several casting processes have been developed to exploit the advantages offered by SSM. However, incorporating SSM into a manufacturing setting is economically challenging, and thus it has for the most part been a niche area of metal forming. In order to understand how and why the semi-solid microstructure is obtained, as well as how to produce it with less expensive methods, much research has been carried out in this field over the past three decades. In recent years, global research into the field has accelerated in the search for ways to fully realize the benefits that semi-solid processing can offer.

The main property of semi-solid metal (“slurry”) that renders it superior to conventional casting processes is the non-turbulent (a.k.a. “laminar” or “thixotropic”) flow behavior that results when one enters the “two-phase” field of solid plus liquid [1]. Specifically, shearing of semi-solid slurry leads to a marked decrease in viscosity, so that a partially frozen alloy can be made to flow like a non-Newtonian fluid. Thixotropic flow behavior arises from the ideal SSM microstructure of small, spherical $\alpha$-Al particles suspended in a liquid matrix. In all semi-solid processes, it is imperative that this microstructure be produced consistently. Moreover, a uniform distribution of this microstructure throughout a volume of slurry is essential for production of high-quality components.

When semi-solid slurry rather than superheated liquid metal is used in a casting process, several advantages are realized [2]. First of all, laminar flow reduces gas
entrainment, which is a problem associated with turbulent melt flow. Laminar flow behavior also allows for the casting of thin-walled sections, which are prevalent in some of the more complex automotive components like steering knuckles and multilink suspensions [3]. Furthermore, since the slurry is lower in temperature than molten metal, die life can be significantly extended by reducing thermal stresses. Solidification shrinkage is also dramatically decreased due to lower processing temperatures. A component cast in an SSM process has improved mechanical properties as a result of lower shrinkage porosity, the absence of entrapped gases, and the enhanced strength of the casting’s non-dendritic microstructure.

Since the early days of development in the 1970’s, many techniques have been devised to cast near-net-shape components with semi-solid slurries [2]. Most of these processes are known as “thixocasting,” in which the semi-solid material is obtained by partially remelting specially prepared feedstock material. Precursor metal for thixocasting does not contain the conventional dendritic microstructure; instead it is comprised of fine, equiaxed primary α-Al particles. Upon partial remelting (“reheating”), the semi-solid microstructure is obtained, and the material can be used in a casting operation. The other approach to semi-solid processing is called “rheocasting,” wherein the slurry is formed directly from the molten state. Also known as “slurry-on-demand” or SoD, rheocasting is the preferred route for the development of new SSM processes, since it eliminates the high cost of specially produced feedstock. Perhaps most importantly, rheocasting is the most logical route to follow for the development of continuous semi-solid casting applications.
The motivation for this work stems from the desire within the SSM community to develop such a continuous slurry-on-demand approach. In order to do this, we must first address the scientific issues that are not fully understood. Recently developed semi-solid forming processes employ some kind of agitation technique to influence the $\alpha$-Al particles to grow in a spheroidal, non-dendritic fashion. While these processes work well, the fundamental mechanisms behind the evolution of SSM structures under these conditions are not well identified [1]. Once the mechanisms are understood, then it will be possible to establish the necessary measures to control the process; this is the most important requirement for scaling up any SoD process.

The questions that need to be addressed in the development of new rheocasting routes are as follows. First, what are the microstructural mechanisms that lead to a well globularized semi-solid microstructure under the imposed conditions of forced convection and copious nucleation? Secondly, how can these mechanisms be manipulated in order to consistently produce high quality semi-solid material in a manufacturing setting? These two issues are addressed in this work, based on experimentation with a new slurry-making technique invented at WPI. This apparatus, called the “Continuous Rheoconversion Process (CRP),” mixes two separate aluminum melts within a reactor, resulting in semi-solid slurries having highly globular particle morphologies. The melt streams undergo forced convection while nuclei are being formed in very high numbers. A thorough microstructural investigation is presented in order to identify the mechanisms at work in this novel solidification process.
2. Background

This section will present a timeline of the important SSM processing routes that have been developed over the last thirty years. General processing aspects of SSM will be described, including the discovery of thixotropic behavior and the differences between thixocasting and rheocasting. Examples of semi-solid methodologies will be presented in detail. Lastly, the pertinent microstructural and solidification paradigms will be laid out in order to provide the context for the present work.

2.1 - History of Semi-Solid Metal Processing

During the course of his PhD research [4], David Spencer documented the initial findings that led to the discovery of semi-solid processing. He was investigating hot tearing in a Sn-15%Pb alloy through the use of a special apparatus that measured the viscosity and shear stress of solidifying metal as a function of fraction solid. This Couette-type viscometer was comprised of two concentric cylinders with an annular space, within which the alloy was allowed to partially solidify. As the outer cylinder was rotated (with the inner one stationary), the material was sheared at various rates, and values for shear stress and viscosity were recorded.

Ironically, the core property of semi-solid processing was discovered during Spencer’s research, which was not related to SSM. In the initial hot tearing experiments, shearing was begun after the metal had begun to solidify, and a predominantly dendritic structure resulted. In an alternate set of experiments, however, shear was imposed on the liquid before solidification began, and continued as the liquid cooled below its liquidus. As a result of this slight modification, the microstructure
became non-dendritic, and the metal behaved quite differently. Specifically, the shear stress (and corresponding viscosity) of the non-dendritic slurry was nearly three orders of magnitude lower than that of the dendritic material - see Figure 1, from [1].

![Figure 1](image)

Figure 1: Viscosity and shear stress vs. fraction solid of (a) dendritic and (b) non-dendritic Sn-15wt%Pb under a continuous shear rate [1].

These findings had important ramifications in terms of the flow behavior of semi-solid metal. At rest, non-dendritic metal slurry behaved as a rigid material in the two-phase region; that is, its viscosity was high enough that it could be handled as a solid. However, when a shear stress was applied, the viscosity decreased dramatically, so that the material behaved more like a liquid [1]. Thus, the slurry could flow in a laminar fashion, with a stable flow front, as opposed to the turbulent flow characteristic of molten metal. The important implication was that this rheological behavior might be exploited to process the metal in completely new ways, and perhaps produce components having superior metallurgical properties [6].
Laminar flow and thixotropy of semi-solid metal are directly related to microstructure. In the shearing of the Pb-Sn alloy in Spencer’s experiments, the microstructure was changed from a dendritic to a non-dendritic morphology. When shear was applied after solidification began, the structure seen in Figure 2a resulted. When shear was applied before solidification began (and continued into the two-phase field), the structure shown in Figure 2b resulted. As mentioned previously, the ideal SSM or “thixotropic” microstructure is comprised of spherical primary particles of small diameter suspended in a liquid matrix. Figure 2b is an example of such a microstructure, from the initial research of SSM at MIT.

![Figure 2: (a) Dendritic structure (quenched at 0.36 fraction solid) resulting from shearing after solidification begins; (b) Non-dendritic structure (quenched at 0.60 fraction solid) resulting from shearing before solidification begins (Alloy: Sn-15%Pb) [5].](image)

It has been suggested [7] that the rounded primary particles seen above tend to agglomerate to form a loosely connected skeletal structure, which gives semi-solid slurry its rigidity when at rest. When shear forces are applied, however, the
agglomerates are broken down as the particles physically move past one another; therefore the viscosity decreases drastically. Once shearing is ceased, the semi-solid material retains its initial viscosity. A plot of this behavior gives a hysteresis loop, which is another unique property seen in SSM. Figure 3 [8] shows a plot of such data, which illustrates how a semi-solid metal is able to recover its solid-like properties after being handled and deformed like a liquid, or more specifically, when shear rates are increased and then decreased. The area enclosed by the curve is a direct measure of the material’s thixotropy.

![Figure 3: Hysteresis loop of shear stress vs. shear rate in semi-solid A357 slurry [8].](image)

The benefits that semi-solid processing holds over conventional liquid metal casting result from the flow behavior of the partially solidified metal. The way in which a metal fills a mold (or die cavity) directly impacts the solidification of the metal; thus, the properties of the formed part can be enhanced with improved mold filling.
Turbulent flow of liquid metal into a die or mold can lead to incorporation of air and mold gases into the melt [2]. This in turn can lead to both macro- and microporosity, which negatively affect the mechanical properties of the final part.

There are several reasons that the laminar flow of semi-solid slurries is very advantageous from a casting standpoint. The first major reason is the elimination of gas entrapment, resulting in decreased porosity and oxide content in the formed part. Secondly, since semi-solid metal has lower heat content than superheated molten metal, there is less solidification shrinkage in the casting. Thus, molds can be filled more effectively and uniformly, and less post-casting machining is required. As a result, all semi-solid processes are potentially “near net-shape” processes. The reduced heat content also lowers the thermal stresses of the casting apparatus (typically a steel die) that contacts the metal, leading to longer tool life. Also, since the starting material has the thixotropic microstructure, the microstructure of any part formed with semi-solid processing is always equiaxed and non-dendritic. The primary $\alpha$-Al particles typically have diameters less than 100$\mu$m. Therefore, the mechanical properties of the final component are better than a similar part formed from a conventional casting process.

The net result of the above-described advantages is that semi-solid casting can be used to produce intricate components with superior mechanical properties. The typical defects associated with molten metal casting can be circumvented when the microstructure (and thus the flow behavior) of the slurry is controlled. From an economic standpoint, it is expected that due to improved tool life, shorter cycle times, reduced machining, and ability to use less expensive heat treatment schedules, semi-solid processes will ultimately become as cost-effective as conventional casting routes.
such as high pressure die casting [9,10]. Perhaps the most attractive attribute of semi-solid forming, however, is that due to the laminar flow of the slurry, very complex shapes can be cast, with thin walled sections on the order of millimeters [3]. Figures 4 and 5 show examples of typical components formed by semi-solid processes.

Figure 4: Transmission belt cover produced by an SSM process [3].

Figure 5: Suspension multilink component produced by an SSM process [3].

Soon after the discovery by Spencer, a number of processes were designed to take advantage of the unique behavior of semi-solid metal slurries. From the very beginning, these processes all devised novel ways to produce the thixotropic
microstructure through some method of vigorous agitation during solidification. It was hypothesized that the induced agitation broke up (or facilitated the melting off of) dendrite arms, which then ripened and spheroidized to form a non-dendritic structure [1]. It soon became apparent that there were two routes for processing semi-solid metal, i.e. two different ways to arrive at the desired point within the solid-liquid, two-phase region. The first route starts from the solid state (“thixocasting”), and the second starts from the liquid state (“rheocasting”). Figure 6 schematically illustrates these two avenues for semi-solid metal formation.

![Figure 6: Schematic of the two major semi-solid processing approaches [2].](image)

Thixocasting processes start out with a solid precursor material (“feedstock”) that has been specially prepared by a billet manufacturer, and then supplied to the casting facility [2]. Feedstock metal has an equiaxed, non-dendritic microstructure. Small amounts or “slugs” of this alloy are partially melted by reheating into the semi-solid temperature range, leading to the thixotropic structure. In most applications, the
slug is subsequently placed directly into a shot sleeve of a die casting apparatus, and the part is formed.

During the initial years of SSM process development, mechanical stirring was used in various ways to break up dendrites and produce thixotropic metal structures [1]. The combination of rapid heat extraction and vigorous melt agitation was effected by using different sizes, shapes, and velocities of stirring rods. Various researchers addressed the evolution of the “stircast” structure during this time [11,12]. Although these methods worked well in that they effectively produced the desired metal structures, erosion of the stirrer became the “weak link” of the process. Focus was placed on the development of “passive” agitation techniques to mitigate stirrer erosion and ensure impurity-free castings [7].

The first highly effective passive method for producing SSM feedstock for thixocasting applications was the Magnetohydrodynamic (MHD) casting process [2]. In this approach, the solidifying melt is not agitated by a mechanical stirrer, but by alternating electromagnetic fields. Induction coils are placed around a crucible to induce these forces. The crucible is equipped with a cooling system to initiate freezing in the alloy while the melt is exposed to the electromagnetic forces. Upon cooling down to ambient temperature, the alloy has an equiaxed, non-dendritic microstructure. The MHD stirring process works remarkably well and is widely used commercially today. Figure 7 presents a semi-solid microstructure typically obtained with the MHD process.
Thixoforming processes comprise the majority of industrial semi-solid applications used today. The main reason for this is the convenience of not requiring melting equipment within the SSM casting facility. However, there are also some disadvantages to thixocasting that may outweigh its benefits. Since billet makers must produce the feedstock material as a service to the SSM caster, there is a significant premium that the caster must pay [9]. Therefore, although MHD is a reliable way to produce SSM feedstock, it is not economical compared to conventional processes. Furthermore, in thixocasting processes, scrap metal must be sent back to the billet manufacturer and cannot be recycled. Most importantly, process control is somewhat difficult in thixocasting, because solid fraction (and corresponding viscosity) is sensitive to temperature gradients in the reheated material. Thus, narrow temperature ranges must be achieved consistently for successful operations. This, combined with the time it takes (several minutes on average) to reheat the feedstock to the desired solid fraction, negatively affects productivity.

Current industrial drive is towards the development of new rheocasting (‘slurry-on-demand’) techniques, wherein the semi-solid slurry is produced directly from the
liquid metal by controlling the solidification path of the alloy within its freezing range. The development of ideal one-step rheocasting applications is highly preferable to the current two- or three-step applications associated with most thixocasting methods [13]. As such, a major goal is to develop a continuous rheocasting process. Thixocasting approaches are inherently batch processes, in which only small amounts of slurry can be produced during each forming operation. This places limits on the sizes and shapes of parts produced in this manner. A continuous process would circumvent these hindrances, and could be used for a broader variety of applications.

Earlier work in the 1980’s that resulted in equiaxed cast structures without breaking up dendrites made use of copious nucleation by casting melts with low superheats. The most popular of these processes was the Microcast-X or “MX” process [2]. In this process, a superalloy melt with a small degree of superheat was poured into a colder mold having a high heat transfer coefficient. Copious nucleation of the primary phase occurred along the wall of this mold, and fluid flow dispersed these nuclei throughout the bulk of the solidifying melt. This method resulted in significant grain refinement, leading to non-dendritic microstructures. Figure 8 shows such a microstructure obtained with this method [2].
Although partial remelting of the sample shown in Figure 8 would result in an SSM structure, this method was not exclusively developed for rheocasting applications. Rather, the developers of the process were striving for improved properties in superalloys via grain refinement [2]. Nevertheless, this is an important consideration when one traces casting developments wherein high nucleation rates were operative. Processes analogous to this such as liquidus casting or low temperature pouring [14,15] also rely on this mechanism for the production of equiaxed structures. Another unique rheocasting approach was developed in the late 1980’s at Southwire Corporation by Chia [2]. Here, equiaxed and fine grain sized copper bars were cast via the Properzi process. Similar to low-temperature pouring, the bars were cast with only 2-4 degrees of superheat. Liquid flow provided convection for seed dispersal, and the low superheat ensured that the seeds did not remelt, but survived in the bulk liquid as grain refining agents.

In the mid-1990’s UBE Industries, Ltd. of Japan introduced the new rheocasting (NRC) process [16], which paved the way for a new class of cost-effective, simple, and
highly effective rheocasting applications. The developers of this technique used the now-popular rheocasting recipe of copious nucleation combined with forced convection to obtain SSM structures. Unlike past processes, dendrites were not broken up in this process; instead, dendritic growth was suppressed from the beginning of solidification. Figure 9 lists the major steps of the NRC process.

![Rheocasting Process Diagram](image_url)

*Figure 9: General steps involved in UBE’s new rheocasting (NRC) process [2].*

As shown in the above Figure, the first step in the process involves achieving adequate control over the temperature of the liquid alloy. Similar to previous liquidus casting techniques, the temperature is kept close to the liquidus. The liquid is poured along a cooling slope or “jig” to induce nucleation, and then along the side of an insulating vessel. Fluid flow within this vessel provides forced convection, dispersing the nuclei throughout the bulk where they can act as further nucleation sites. Next, air is blasted against the sides of the crucible, and heat transfer is allowed to occur only through the sides of the vessel. As the resulting slurry cools through the SSM range, the heat content in the vessel is adjusted with heaters to arrive at the desired solid fraction. When the slurry is ready for processing, the vessel is inverted, the metal drops into a
shot cavity, and the component is formed. Figure 10 is a microstructure of SSM material obtained with the UBE process.

![Microstructure](image)

Figure 10: Typical microstructure obtained with the UBE process. Alloy: Al-Si-Cu [2].

The above description is a generalized one, since the UBE patent [16] extends these solidification ideas to several other potential SSM processing routes. Each of the techniques listed in the patent follows the general procedure outlined above. That is, heat extraction and forced convection are induced in order to spheroidize the primary particles and obtain thixotropic slurry structures. The NRC process is used solely for rheocasting or SoD applications, but it is a batch process, not a continuous one. Since relatively small vessels are used, only one shot per vessel is attainable. Nonetheless it has been successfully implemented in industrial settings.

A similar continuous semi-solid casting process was recently reported by researchers at the Chiba Institute of Technology in Japan [17]. Here, an inclined plate is utilized to nucleate $\alpha$-Al from an aluminum melt with varying levels of superheat. The
flow of liquid along the plate disperses the nuclei throughout the bulk liquid, resulting in a high level of grain refinement in the solidified samples. In the work, a wrought alloy (Al-1.63mass%Si-0.54mass%Mg) was produced for thixocasting applications. Average particle size in the most refined samples is about 60µm. Moreover, by varying the process conditions, the researchers showed that both dendritic and non-dendritic morphologies could be attained and correlated to the mechanism described above.

In the recent past, through the SSM consortium established at WPI, colleagues at MIT developed a new slurry-on-demand process, which was named the Semi-Solid Rheocasting (SSR) process [2,18,19]. The three basic steps in this process, illustrated in Figure 11, are as follows: (1) the melt experiences a short period of agitation as it cools through its liquidus, (2) localized heat extraction is effected by the rotating “cold finger,” and (3) the low solid fraction slurry is cooled slowly to a desired solid fraction.

Figure 11: (a) Illustration of the steps involved in the SSR process (b) Typical thermal history of SSR-processed slurry [2].
The SSR process results in highly globularized semi-solid slurries, as seen below in Figure 12. The combined stirring and cooling of the melt causes the primary-phase particles to grow non-dendritically, as in the UBE process. Figure 11(a) is closely drawn to scale, which implies that the amount of slurry per run that can be created in the laboratory-scale version of the apparatus limits the process to batch-type applications. To scale it up, the licensing rights to the SSR process were acquired by IdraPrince Inc. (a subsidiary of IdraPresse, SpA), and commercialization of the technique is currently being carried out [20].

![Microstructure of slurry produced using the SSR process. Alloy: A356 [2].](image)

At around the same time that the SSR process was developed, research was carried out by Nasim Alem at WPI [21] in which several novel methods for grain refining aluminum casting alloys were investigated. In one of these experiments, two liquids were mixed together very close to their liquidus temperature. One alloy was A356, and the other was an industrially developed alloy called SiBloy®, containing non-fading or “permanent” grain refinement agents. After pouring one crucible of liquid
SiBloy® into a crucible of A356, a cold graphite stirrer was used to induce convection and copious nucleation. The “product melt” was cooled quickly through its liquidus temperature, as seen in Figure 13, which is the temperature-time profile recorded in the experiment.

![Temperature-time profile](image)

*Figure 13: Time-temperature data from original liquid mixing experiment by Nasim Alem [21].*

By forming a high number of nuclei and distributing them throughout the bulk by vigorous stirring, a highly grain refined structure was produced. Figure 14 shows this microstructure, from a sample that was anodized to highlight the different grain orientations.
Figure 14: Microstructure obtained from original liquid mixing experiment by Nasim Alem [21].

As seen in the above Figure, the microstructure is non-dendritic, equiaxed, and contains small primary $\alpha$-Al particles. Since a heat-extracting stirrer was used in this experiment, the mechanism leading to this structure is similar to that present in stircast structures (see [11,12]); however there is additional convection (via fluid flow) present from mixing the two melts together just prior to stirring. Therefore, it was hypothesized that the mixing of two liquid melts, when intensity of convection and temperature change is adequately controlled, results in a high level of grain refinement. This should not be confused with chemical grain refining, which has also been proposed as a method to produce thixotropic microstructures [2].

It has been shown repeatedly [2,22,23] that upon reheating into the semi-solid temperature range, a refined and equiaxed morphology of primary particles will evolve to form the SSM microstructure. Therefore it is realistic to assume that a process employing the experimental conditions imposed by Alem will also form excellent SSM feedstock materials. It is thus concluded that such a process should form thixotropic microstructures directly from the molten state.
In addition to the processes described above, some other successful rheocasting processes have been developed over the years in which different approaches to SSM structure formation are used. In one such technique, known as the SLC® (sub-liquidus casting) process, melt agitation is not induced; instead, the process relies on close control over temperature in an undercooled melt to attain SSM structures [24]. This process was developed by THT Presses, Inc., and is currently used as a low-cost alternative to conventional SSM processes such as MHD stirring. Figure 15 is a microstructure produced with the SLC process, from unpublished research at MPI.

![SSM microstructure obtained with the SLC process. Alloy: A356](image)

*Figure 15: SSM microstructure obtained with the SLC process. Alloy: A356 [25].*

In another method, melt agitation is not attained with mechanical means, but with a passive mixing technique. The process was developed at the Fiat Research Center in Orbassano, Italy, in the mid-1980’s [26]. A “static mixer” is employed, comprised of a series of alternating right-hand and left-hand helicals made of a material with a high conductivity. As a result, high levels of shear are induced in the alloy melt as heat is extracted by the helicals. The process works quite well and results in slurries
having low viscosities at relatively high solid fractions. However, the equipment associated with the process is rather complicated, since two separate electromagnetic pumps are required to induce melt flow [26]. Thus, although the technique seems to work well for the authors’ particular manufacturing setting, it may not be a cost-competitive route for wider-ranging rheocasting applications. Nonetheless, the concept of passive melt agitation is still a promising one for the development of simpler, less expensive slurry-making processes.

The presentation of the above semi-solid processing technologies has laid the groundwork for the introduction of a new approach to continuous rheocasting. It has been shown that the most effective processes for the production of the thixotropic microstructure combine copious nucleation with forced convection to achieve non-dendritic, spherical particle morphologies. However, to date, none of these processes have satisfactorily addressed the need for a continuous semi-solid casting route. The current need in the SSM field is to devise a relatively simple, easy-to-implement, flexible process that can be used for a wide variety of processing applications. Such a process should use novel and relatively simple methods of melt agitation to avoid the problems associated with the previously discussed approaches. The research approach for the present work will be outlined shortly, but first the mechanisms governing SSM structure formation will be briefly reviewed.
2.2 – Previously proposed mechanisms for SSM structure formation

The most important factor in all SSM processes is microstructure control, as it directly impacts all other pertinent parameters of the metal slurry. As such, it is imperative that the mechanisms that lead to the formation of the SSM structure be well understood. The conditions that lead to suppression of dendritic growth in the processes discussed above, namely copious nucleation followed immediately by forced convection throughout the bulk of the melt, are not yet bound by a cohesive mechanistic theory. Previously proposed mechanisms in the research field will be covered here in order to provide the context for understanding the need for such a theory.

In the early days of SSM research at MIT, it was thought that dendrites had to be broken up in order to yield thixotropic structures. Several mechanisms for this were theorized and reported [7,11], and experimental evidence through most of the 1980’s supported these mechanisms. However, it has become clear that one can eliminate the need for breaking up dendrites by suppressing dendritic growth from the very start of solidification. The SSR developers [18] state that this is possible by achieving a very high cooling rate through the liquidus combined with forced convection. Agitation of the melt need only occur during the initial stage (i.e. 1-2 vol% solid) of solidification, since all particles form at or just below the liquidus temperature. After this initial burst of nucleation, the particles coarsen to give a fine thixotropic microstructure. The NRC process also suppresses dendritic growth by following a similar method.

In recent studies at Brunel University [27] using a novel twin-screw “rheoextruder,” important findings regarding the evolution of the SSM structure under forced convection have surfaced. In this patented device, a mechanical stirrer of
complex geometry is employed to induce varying levels of shear and turbulence in a solidifying alloy. The design of the apparatus allows for nucleation of the primary phase throughout the melt via several cooling channels placed at various points in the melt holding vessel. The alloy used in these studies is the model alloy Sn-15wt%Pb. The researchers characterized the effects of forced convection and turbulence on homogeneous nucleation of the primary phase throughout the bulk of a large volume of molten metal. Highly globular structures were obtained with the apparatus, and dendritic growth was totally suppressed. Figure 16 from [27] represents these microstructural findings.

Figure 16: Sn-15wt%Pb alloy continuously sheared at 3625s\(^{-1}\) in a twin-screw extruder, and quenched at 13°C below its liquidus temperature [27].

It was concluded that by ensuring uniform temperature and composition fields throughout the bulk of the melt, the effective nucleation rate was maximized [27]. That
is, copious nucleation of the primary phase was induced throughout the melt, and all of these nuclei survived because the liquid was not locally hot enough to remelt them. Also, the mixing action of the device dispersed these particles throughout the bulk melt to act as further nucleation sites. Furthermore, the Brunel researchers proposed that the mechanisms leading to spherical growth of the primary particles under forced convection and turbulence have to do with stabilization of the solid/liquid interface. The mechanism agrees well with the experimental results obtained in the work, but it has not been verified with aluminum alloys as of yet. Furthermore, it is very difficult to validate the theoretical aspects such as reduced boundary layers and increased gradients with experimental data. The major conclusion of the work was that increasing shear rate and nucleation rate led to the promotion of spherical growth of the primary phase.

A similar explanation for cellular growth of particles in a stircast application was given by Molenaar, et al. [12], in which it was reported that fluid flow lowers the solute gradient ahead of the S/L interface of a floating particle. This relationship between diffusion boundary layers and spherical growth was also predicted by Doherty [11]. He proposed that when there is a high density of nuclei growing, their diffusion boundary layers overlap with one another. Thus, the compositional gradients are reduced, leading to a suppression of the instabilities that typically result in dendritic growth. Finally, the Mullins-Sekerka criterion [28] asserts that when there is a low undercooling and a high amount of nucleation sites in a solidifying alloy, an equiaxed structure is most likely to form. Therefore the findings by Fan and Ji have strong support in past experimental work. The effect of S/L interface stability by forced
convection and turbulence in a solidifying melt certainly warrants more attention so that the mechanism can be verified and understood for Al alloys.

3. Research Approach

From this review it is clear that there is a need for a robust, all-encompassing rheocasting route that can fully realize all of the advantages of semi-solid metal forming. Several processes have been developed in the last three decades in attempts to fully benefit from SSM’s thixotropic behavior. While impressive in their scope, clever in their designs, and effective in their particular niche, most industrially employed techniques simply impose limits on what (as well as how much, how quickly, and how efficiently) can be produced. A continuous rheocasting process is theoretically the best way to incorporate SSM into the metals forming industries for multifaceted, diverse manufacturing programs. Moreover, the need remains to address lingering confusion regarding semi-solid structure mechanisms under forced convection. All recent efforts induce agitation at the beginning of melt crystallization, but the reasons why such agitation makes the floating particles grow like spheres rather than dendrites are not suitably understood.

The hypothesis behind the liquid mixing technique for SSM slurry formation is as follows. *Copious nucleation of the primary phase during the early stages of solidification coupled with forced convection due to complex fluid flow can result in the formation of thixotropic SSM structures.* By imposing uniform temperature distributions, it is possible to maximize effective nucleation rates in the solidifying bulk liquid; i.e., this condition ensures nuclei “survival.” These nuclei are dispersed
throughout the bulk liquid by convective currents, where they can (a) act as further nucleation sites and (b) contribute to a homogeneously thixotropic microstructure. When very high numbers of nuclei are formed and do not remelt, the growth of the particles is limited, since there is simply no space available for the particles to grow into. Moreover, by limiting growth, it is ensured that the initial morphologies of the nuclei remain unaffected; therefore if enough of the nuclei initially grow spherically, then overall dendritic growth can be suppressed throughout the alloy.

How does the controlled mixing of two liquid alloy melts create the above conditions? The premise is to remove heat from the metal streams uniformly, at exactly the same time as they combine within a mixing reactor. Rapid heat extraction results in copious nucleation, whereas fluid flow through complex channels forces convection in the melt streams. By nucleating large amounts of $\alpha$-Al on the heat-extracting inner walls of this reactor while fluid flows through the channels, dispersion of the crystal seeds results. Uniformity of the temperature distribution can be ensured by keeping the reactor’s channel diameter relatively small. This is further realized by tight control over the temperatures of the melts immediately prior to mixing. In the next section, the experimental apparatus will be presented in detail. In addition to supplying very interesting experimental results, this laboratory apparatus holds promise as a precursor to a fully continuous rheocasting process.
4. Experimental Methodology

The discussion of experimental methodology is divided into three sections. In the first section, the liquid mixing apparatus used for this work, also known as the “Continuous Rheoconversion Process” or CRP, will be presented. In the second section, the experimental plan will be reviewed. Finally, the procedures followed in each liquid mixing experiment will be detailed, from preparation to the alloy charges to metallographic analysis.

4.1 – The Continuous Rheoconversion Process (CRP)

4.1.1 - The Apparatus

The CRP is a relatively simple process that takes two liquids, held at a particular level of superheat, and passively mixes them together within a reactor that provides forced convection and rapid heat extraction. In terms of commercial applicability, the projected advantages of the process include process simplicity, flexibility, tight control over SSM structure evolution, fast adjustment of solid fraction, and incorporation of scrap metal for recycling. The term “flexibility” refers to the ability of the process to be used for both thixocasting and rheocasting applications. Before building the device, the following illustrative schematic was created, shown in Figure 17. The reactor design shown here is not the one that was ultimately used; it is only intended to illustrate the concept of a “tortuous path” to induce forced convection.
As seen in Figure 17, the major characteristics of the CRP apparatus include independent temperature control of each precursor alloy melt, a heated channel system to transport the melts without any heat loss, and a reactor to (a) provide copious nucleation and (b) induce forced convection in the melts as they flow through it. The reactor can be preheated to vary its heat extraction capability.

The above diagram is intended to provide the reader with the basic variables inherent to the design of the device. These parameters include but are not limited to independent control over the heat content of the melts, the chemical composition of each melt, and the rate at which heat is extracted from the “product melt” within the reactor. Figure 18 is a photograph of the CRP apparatus.
With Figure 18 as a guide, the liquid mixing apparatus will now be described. The frame was constructed of aluminum Unistrut® beams, and casters were installed to make the device mobile. Aluminum sheeting was used to compartmentalize the electrical control cabinet. Two 6” diameter, 12” high resistance tube furnaces were placed in sheet steel housings and insulated with Fiberfrax® insulation material. These are the melting furnaces. Within each of these furnaces, a crucible-holding setup was constructed, consisting of two top and bottom steel rings connected to two threaded rods that run vertically through the furnaces. These rods connect to a Unistrut® beam above the furnaces, and are anchored to 4” diameter ring plates, which are in contact with the
The bottoms of the furnaces. The steel rings clamp the crucible in place, and the rods are put in tension so that the crucibles do not contact the furnace element.

The bottoms of the clay-graphite crucibles have threaded 1” holes tapped into them. A “spout” component screws into these holes and extends about an inch from the bottom of the crucible. The exit hole through which the metal flows is ½” in diameter. A ½” diameter stopper rod plugs the hole during melting and temperature stabilization of the alloy charge. The rod and the spout were both made from hot-pressed Boron Nitride (BN). Figure 19 presents two photographs of this configuration.

![Figure 19: (a) Stopper rod and exit spout; (b) a top-down view of the crucible within the melting furnace, showing the pull-action solenoid.](image)

The stopper rod is connected to a pull-action solenoid that is connected to the overhead beam. Both of the solenoids are wired to a toggle switch. When the switch is thrown, the plugs are pulled from the exit spout, and the liquid metal flows from the exit holes of each crucible at the same time. Since each crucible is in a separate furnace, the
temperatures can be independently controlled and monitored so that the heat contents of the melts upon mixing are precisely known.

The space beneath the melting furnaces is comprised of heated runners that transport the melt streams to the reactor. These runners are 1” diameter steel conduit tubes with a straightaway length of about 15” and an angled length of about 4.” Several coats of insulating BN coating are applied to the insides of the tubes. In order to prevent heat loss of the flowing melts during transport, these conduits are heated to ten degrees above the melts’ temperatures using coiled heating elements, shown below in Figure 20. (Appendix B presents results from two “control experiments,” wherein it was microstructurally ascertained that no heat loss occurred in these tubes.) These elements ensure a uniform temperature distribution along the entire lengths of the tubes. They are designed to slip easily over the tubes while still contacting the outer surfaces. For insulation, Fiberfrax® blanket is wrapped tightly around the tubes prior to an experiment. The temperature is controlled using a thermocouple placed in direct contact with the tube.

Figure 20: Coiled heating elements used for heating the liquid metal transport tubes.
At the entrance of the reactor, there is a steel “boot” component that fits around the tubes. It has two functions: to change the angle and diameter of incoming liquid to match that of the reactor passages; and to prevent welding of the aluminum to the entrance bays of the reactor. The boot is coated with BN and placed in contact with the tube heaters in order to prevent premature solidification of the melts. Figure 21 is a photograph of the boot component.

![Figure 21: “Boot” component of the CRP.](image)

Two reactors were used in this study: a preliminary one used for the trial runs of the apparatus, and a secondary one used for the remainder of the work. The reactors were machined from square copper blocks, 3” square and 6” in height. The diameters of the inner channels are ½”. Figure 22 shows the designs of the two reactors.
It was important to ensure that the preliminary reactor effectively mixed the melt streams, and that convection forces were in place. Therefore a similitude experiment was carried out in which two water streams containing different colored dyes were mixed within the preliminary reactor. Plexiglas® was placed over the face of the reactor and the experiment was recorded with a video camera. Based on this experiment, it was determined that adequate mixing took place within the reactor. It was thus concluded that molten aluminum flowing through the reactor experiences forced convection due to interaction of the two liquids streams.

In the second reactor, angled paths were again used, but with a different, more symmetric design. In order to verify that the second reactor provided forced convection, another similitude experiment was carried out using the same procedure outlined above. The experiment indeed showed this to be the case, so the design was kept as a constant parameter in this study. In future work, this variable will be explored using mathematic modeling to characterize and optimize the reactor’s mixing capability.

*Figure 22: Inner designs of the preliminary (left) and secondary (right) mixing reactors.*
As seen in Figure 22, the copper block was split in half along the vertical direction. The inner machining was done using a computer-guided end mill. Holes were tapped in the two faces so that the block could be clamped together with hexagonal screws. The inner faces of the reactor were coated with graphite spray to improve melt flow. Four small thermocouple holes were also endmilled at various points of the mixing channel in order to record the temperatures of the flowing melt streams at various points of the process. Finally, two support arms were constructed to connect to the top of the reactor, allowing for the reactor to be placed within a preheating furnace. A photograph of this particular setup is shown below in Figure 23.

![Figure 23: Setup of the third furnace when the reactor is preheated.](image)

When the above configuration is not used, the reactor sits on two parallel Unistrut® beams, set at an appropriate height to connect to the transport tubes. The receiving crucible is placed as close to the reactor’s exit as possible to minimize turbulence in the product slurry as it fills the receptacle.
There are three combinations of the above-described components used in the experiments. The third mobile resistance furnace (of 6” inner diameter and 6” height) can be used in two ways. In one configuration, the reactor is suspended within the furnace and preheated so that its heat extraction capability is varied. The low solid fraction slurry that exits the reactor is then deposited into a clay-graphite crucible and cooled in air.

The second configuration allows for the receiving crucible to be placed within the third furnace, where its temperature can be set before an experiment takes place. This is the direct rheoconversion application of the CRP, because the product slurry that exits the reactor is deposited into a heated receptacle. Therefore the slurry can be cooled very slowly through its SSM temperature range, and small amounts can be removed and quenched to observe the microstructure.

The third and final configuration does not employ the third furnace at all, but converts the liquid to slurry using an unheated reactor. The slurry is then deposited into a unheated receiving crucible, where it solidifies in air.
4.1.2 – Process Variables

Now that the liquid mixing device has been fully described, the variables that were studied will be discussed. In any process there are two kinds of variables: independent and dependent. The independent variables are those that can be changed by applying different experimental conditions, whereas the dependent variables are dictated by the imposed conditions. In this study, there are only two dependent variables: (a) the microstructure of the samples obtained in any given experiment and (b) the temperature of the low solid fraction slurry that exits the mixing reactor. If further processing were done to the slurry, such as rheological measurements or mechanical testing of cast samples, then these too would be dependent variables that could be correlated to the imposed conditions of an experiment.

On the other hand, there are several independent variables that can be changed due to the design of the CRP apparatus. The most important is the heat content in the precursor melts. Since the two furnaces independently control each melt, this variable is tightly controlled. Another independent variable is melt chemistry. Separate starting vessels make available the option of using alloys of different compositions. For example, one could mix a melt containing grain-refining additions with one containing no grain refiners. Another example is to have a master alloy in one vessel and a pure metal in the other, and mix them together to form a third alloy of a desired composition. The heat extracting capability of the reactor is an independent variable, since the reactor can be preheated prior to melt mixing. The degree of heat extraction corresponds to the nucleation rate induced in the solidifying melt stream. The temperature of the receiving crucible is also an independent variable, and can be varied to observe the effect of
cooling rate on the structural evolution in the collected slurry. Finally, when the receiving crucible is preheated, the cooling rate of the slurry can be controlled by varying the crucible temperature. Other sample collection methods to be described shortly can also affect cooling rate, which directly impacts the microstructural evolution.

There are also a few independent variables that were not explored in this study. The first is velocity of the melts as they flow into the reactor. Since the lengths of the melt transport tubes (and the angles at which they are bent) were kept constant, velocity was not varied. This variable warrants further attention, since it may affect the level of forced convection in the reactor. Also, since only two reactor designs were used, the forced convection due to the inner channel design was not changed appreciably. In future studies, different reactor designs will be employed to address this important parameter. Finally, in all experiments, the temperatures of the two precursor melts were kept equal to influence uniform temperature fields within the reactor. When two different alloy systems are used in the CRP, their temperature difference (due to different liquidus points) becomes another potential variable.

4.2 - Experimental Plan

The layout of this section is as follows. First, the preliminary work carried out will be discussed. The two subsequent sections address two important variables: the alloys used in the CRP and method of slurry collection and analysis. Next, the experiments carried out in the work will be described. The description of the experiments is separated into five sections, corresponding to two thixocasting subsets and three rheocasting subsets.
4.2.1 – Preliminary work

As mentioned previously, the impetus for this work came from a liquid mixing experiment performed by Nasim Alem during her investigation into novel grain refinement methods. The first task carried out was to reheat that sample into the semi-solid temperature range and quench it in water. The purpose was to verify that the equiaxed structure obtained in her experiment would evolve to a thixotropic structure upon partial remelting. Subsequent to this, verification of the first liquid mixing experiment was performed, using the same methods carried out by Alem.

Once the apparatus was constructed, there were several trial runs carried out. Only the superheats of the melts were varied in these experiments, and they were kept to within a few degrees of the liquidus temperature. The intent of these runs was to test the equipment, determine if any modifications were needed, and ensure that the apparatus consistently produced thixotropic structures.

4.2.2 – Alloys used

The three alloys used were A356.2 (with no grain refiners), A356.2 (with TiB₂ grain refiners), and SiBloy®, which contains permanent grain refiners in the form of AlB₂ particles. Table 1 gives the chemical compositions and liquidus temperatures of each of these alloys. Chemical compositions were obtained with a Spectromax® spectrographic analysis machine. Liquidus temperatures were determined with the derivative method on data collected in cooling experiments using calibrated thermocouples.
Table 1: Chemical compositions (wt%) and liquidus temperatures (°C) of the alloys used.

<table>
<thead>
<tr>
<th></th>
<th>T_L</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ti</th>
<th>Sr</th>
<th>V</th>
<th>B</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A356.2 (NGR) - without GR</td>
<td>616.2</td>
<td>6.82</td>
<td>0.07</td>
<td>0</td>
<td>0.324</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
<td>0.006</td>
<td>0.001</td>
<td>Bal.</td>
</tr>
<tr>
<td>A356.2 (GR) – with GR</td>
<td>615.5</td>
<td>6.87</td>
<td>0.06</td>
<td>0</td>
<td>0.36</td>
<td>0.11</td>
<td>&lt;0.001</td>
<td>0.008</td>
<td>0.0005</td>
<td>Bal.</td>
</tr>
<tr>
<td>SiBloy®</td>
<td>616.0</td>
<td>6.83</td>
<td>0.08</td>
<td>0.02</td>
<td>0.291</td>
<td>0.003</td>
<td>0</td>
<td>0.001</td>
<td>0.016</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The first stock of A356.2 alloy had a negligible Ti content, and thus was absent of grain refinement. This alloy was used solely in the thixocasting experiments. A second supply of A356.2 alloy had TiB₂ (“TiBor”) grain refiners present. The third alloy used, SiBloy®, is a permanently grain refined alloy containing AlB₂ particles in the molten state. SiBloy® was only used for one experiment in order to compare its grain refinement to that of A356.2 with TiBor. The grain-refined alloys were used only in the rheocasting experiments. A batch of A356.2 with no titanium was prepared for the final experiment, in which slurry structures from grain-refined and non-grain-refined alloys were compared.
4.2.3 – Slurry collection method

Two methods of slurry collection and analysis were followed. In the first method, the slurry was solidified in air within a clay-graphite crucible, after which small samples were reheated into the SSM range and quenched. This is termed the thixocasting set, and its purpose was to verify exploratory findings, as well as to study the microstructural evolution of the as-solidified samples upon partial remelting.

In the second method, the product slurry did not solidify to give a thixocast sample, but rather simulated the “slurry-on-demand” method. In these experiments, which comprise the rheocasting set, the slurry was collected and quenched into water at various temperatures within the two-phase range of the alloy. Three distinct methods of collecting the rheocast slurry were used in the rheocasting set of experiments. In the first method, slurry was quenched immediately into water without entering a crucible. In the second technique, a heated receiving crucible was employed from which small amounts of the slurry were removed (scooped out) at various times and quenched in water. In the third approach, the entire slurry crucible was quenched in water at a single temperature in the two-phase field. By changing the temperature of the receiving crucible, the cooling rates of the received slurry were varied. Figure 24 is a schematic that illustrates the solidification paths induced in these two sets of experiments. Figure 25 is a flow chart that shows in detail the sample collection methods.
Figure 24: Schematic diagrams detailing the solidification paths undergone in the two experimental phases. Arrows indicate quenching of slurry.
4.2.4 – Thixocasting experiments: Variable thermal conditions

Heat transfer conditions in the reactor were affected but varying two parameters: melt superheat and reactor temperature. In the first set of thixocasting experiments (denoted “T1”), the superheats of the precursor melts were varied from 1-64°C in order to gauge the heat extraction capability of the reactor. The reactor was kept at room temperature. Table 2 lists these experiments. “T_{IN}” refers to the temperature of each melt prior to mixing.
Table 2: Experiments carried out in the “T1” series.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>( T_{IN} ) (°C)</th>
<th>Mass/melt (g)</th>
<th>Alloy</th>
<th>( T_{reactor} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1-1</td>
<td>617</td>
<td>300</td>
<td>A356.2 (NGR)</td>
<td>32</td>
</tr>
<tr>
<td>T1-2</td>
<td>625</td>
<td>300</td>
<td>A356.2 (NGR)</td>
<td>32</td>
</tr>
<tr>
<td>T1-3</td>
<td>640</td>
<td>300</td>
<td>A356.2 (NGR)</td>
<td>32</td>
</tr>
<tr>
<td>T1-4</td>
<td>660</td>
<td>300</td>
<td>A356.2 (NGR)</td>
<td>32</td>
</tr>
<tr>
<td>T1-5</td>
<td>680</td>
<td>300</td>
<td>A356.2 (NGR)</td>
<td>32</td>
</tr>
</tbody>
</table>

In the second set of thixocasting experiments (denoted “T2”), three superheats and three reactor temperatures were chosen to observe the effects of different heat transfer conditions on the resultant structures. The reactor was placed within the third furnace, and four thermocouples were inserted into the thermocouple holes to monitor its temperature. An increase in reactor temperature decreases the heat extraction rate of the melts as they flow through it. Therefore the nucleation rate of the combined melts is also decreased. The receiving crucible was at ambient temperature upon collection of the slurry. A thermocouple placed in the exit channel recorded the slurry’s exit temperature. Table 3 lists the experiments carried out with this configuration.

Table 3: Experiments carried out in the “T2” series.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>( T_{MIX} ) (°C)</th>
<th>( T_{reactor} ) (°C)</th>
<th>Alloy</th>
<th>Mass/melt (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2-1</td>
<td>625</td>
<td>130</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
<tr>
<td>T2-2</td>
<td>625</td>
<td>315</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
<tr>
<td>T2-3</td>
<td>625</td>
<td>500</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
<tr>
<td>T2-4</td>
<td>640</td>
<td>130</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
<tr>
<td>T2-5</td>
<td>640</td>
<td>315</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
<tr>
<td>T2-6</td>
<td>640</td>
<td>500</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
<tr>
<td>T2-7</td>
<td>655</td>
<td>130</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
<tr>
<td>T2-8</td>
<td>655</td>
<td>315</td>
<td>A356.2 (NGR)</td>
<td>300</td>
</tr>
</tbody>
</table>
4.2.5 – *Rheocasting experiments: Immediately quenched slurry*

Two experiments were carried out to observe the structure of the low solid fraction slurry immediately upon exiting the reactor. A large reservoir of cold water was used as a receptacle. This resulted in a very high cooling rate in the collected slurry. The first of these experiments was done at a temperature of 625°C, and the second at 640°C. All other conditions were identical to those in experiment T1-2 (see Table 3). These experiments are denoted “R1.”

4.2.6 – *Rheocasting experiments: Various slurry collection temperatures*

The next stage in the project involved the direct collection of semi-solid slurry. Using the third furnace, the receiving crucible was preheated to various temperatures. After slurry collection, small amounts were scooped out from the receptacle and quenched in water. The reactor was kept at ambient temperature for each of these experiments. The first phase of these experiments, denoted “R2,” is listed in Table 4.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$T_{MIX}$ (°C)</th>
<th>$T_{cruc}$ (°C)</th>
<th>Alloy</th>
<th>Samples taken at (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R2-1</td>
<td>640</td>
<td>585</td>
<td>A356.2 (GR)</td>
<td>597, 590, 585, 575, RT</td>
</tr>
<tr>
<td>R2-2</td>
<td>655</td>
<td>585</td>
<td>A356.2 (GR)</td>
<td>605, 597, 590, 585, 575, RT</td>
</tr>
<tr>
<td>R2-3</td>
<td>625</td>
<td>585</td>
<td>A356.2 (GR)</td>
<td>610, 605, 597, 590, 585, 575, RT</td>
</tr>
<tr>
<td>R2-4</td>
<td>670</td>
<td>585</td>
<td>A356.2 (GR)</td>
<td>610, 597, 590, 585, 575, RT</td>
</tr>
<tr>
<td>R2-5</td>
<td>625</td>
<td>450</td>
<td>A356.2 (GR)</td>
<td>610, 600, 590, RT</td>
</tr>
<tr>
<td>R2-6</td>
<td>625</td>
<td>450</td>
<td>SiBloy®</td>
<td>610, 600, 590, 580, RT</td>
</tr>
<tr>
<td>R2-7</td>
<td>625</td>
<td>450</td>
<td>A356.2 (NGR)</td>
<td>600, 590, 580, RT</td>
</tr>
</tbody>
</table>
In the first five of the above experiments, the A356.2 (GR) alloy described in Table 1 was used. The higher level of titanium in this alloy resulted in grain refinement, whereas the alloy used in all previous experiments had negligible titanium. Experiments R2-5 and R2-6 sought to compare the structures obtained with different grain refining agents. R2-5 (A356.2 with 0.11wt%Ti) had TiB$_2$ particles present in the melt, whereas R2-6 (SiBloy®) had AlB$_2$ inoculants. Finally, R2-7 employed A356.2 with no grain refiners, in order to compare the results to those obtained with inoculants present. Since two different crucible temperatures (585°C and 450°C) were used in the experiments, different cooling rates of the slurry through the two-phase field resulted. In all experiments the mass of each charge was approximately 300g.

4.2.7 – Rheocasting experiments: Single slurry collection temperature

In an alternative approach, different preheat temperatures in the receiving crucible were used to attain different cooling rates of the product slurry through the two-phase region. Furthermore, the entire slurry crucible was quenched in a large volume of water, rather than removing small amounts at iterated times. This gave a more accurate sense of the temperature of the sample upon quenching. In the R2 experiments, the thermocouple was not always in the same area as the slurry samples that were removed and quenched, so there was a slight uncertainty in temperature. These experiments, denoted “R3,” are summarized in Table 5.
Table 5: Experiments carried out in the “R3” series.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>(T_{\text{MIX}}) (°C)</th>
<th>(T_{\text{crucible}}) (°C)</th>
<th>Alloy</th>
<th>Mass/melt (g)</th>
<th>Sample(s) taken at (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R3-1</td>
<td>625</td>
<td>100</td>
<td>A356.2 (GR)</td>
<td>300</td>
<td>588</td>
</tr>
<tr>
<td>R3-2</td>
<td>625</td>
<td>200</td>
<td>A356.2 (GR)</td>
<td>300</td>
<td>585</td>
</tr>
<tr>
<td>R3-3</td>
<td>620</td>
<td>200</td>
<td>A356.2 (GR)</td>
<td>300</td>
<td>585</td>
</tr>
<tr>
<td>R3-4*</td>
<td>625</td>
<td>500</td>
<td>A356.2 (GR)</td>
<td>300</td>
<td>585</td>
</tr>
<tr>
<td>R3-5</td>
<td>625</td>
<td>500</td>
<td>A356.2 (GR)</td>
<td>300</td>
<td>585</td>
</tr>
</tbody>
</table>

As seen in Table 5, the main variable was the receiving crucible temperature, which led to different cooling rates of the slurry through the two-phase field. R3-4 is marked because only one melt was used in order to observe the theoretical effect of less convection (due to less liquid mixing) on the resultant structures.

4.3 - Experimental Procedures

This section outlines the steps taken in performing the liquid mixing experiments. The procedure for verification of Alem’s experiment was as follows. Two separate crucibles were heated in resistance box furnaces, each containing about 1 lb. of alloy. One crucible contained A356.2 (no grain refiners) and the other contained SiBloy®. After melting, the crucibles were removed from the furnaces and allowed to cool to 617°C and 622°C, respectively. At this point, the crucible containing SiBloy® was poured into the A356.2-containing crucible. A cold graphite rod, 1” in diameter, was used to stir the melt mixture. Stirring with this material resulted in a rapid cooling rate of through the liquidus temperature, and forced convection to disperse the nuclei. The final melt was then allowed to solidify in air. A small sample (about 5g) of this alloy was reheated to 585°C, held there for several minutes, and quenched in water to
retain the semi-solid microstructure. Metallographic analysis of both the “as-solidified” and reheated samples was carried out.

The procedure for using the liquid mixing apparatus is as follows. First, the reactor is prepared by spraying a coating of graphite onto the inner surface. When used at ambient temperature, the reactor is placed onto two Unistrut® beams, after which the melt transport tubes are put into place. When preheated, the positions of the beams are modified to hold the preheating furnace. The reactor is placed within the furnace using two support arms, as was shown in Figure 23, and its temperature is monitored with four K-type thermocouples.

The crucible assembly is not removed from the apparatus unless maintenance is required, so the next step is to connect the melt transport tubes from the reactor entrance to the crucible spouts. The coiled heating elements are placed around the tubes before this step. Insulation is wrapped around the tubes and placed into the bottom holes of the melting furnace. The control thermocouple for the transport tubes is inserted into the insulation layer so that it touches the surface of the tube. The receiving crucible contains a thermocouple with a stainless steel protection tube to record the temperature of the slurry upon exiting the reactor.

In the thixocasting experiments, the receiving crucible sits just below the exit of the reactor. In the R1 experiments, a large volume of water is used rather than a crucible to immediately quench the slurry. For the R2 and R3 experiments, the crucible is preheated within the third furnace. A preheated graphite “slurry-scooping” utensil is employed to take out small amounts of slurry and quench them in water.
The next step is to place the alloy charges, about 300g each, into the melting crucibles. Thermocouples are inserted into these crucibles to monitor and record the temperatures of the separate melts, and insulating material is placed atop the furnaces. Melting of the charges occurs after about a half hour, with a setpoint of 750°C-800°C. The temperatures of the transport tubes are set to 10°C above the precursor melts’ temperatures. Temperature data is recorded using a data acquisition system and DasyLab® software. After the melts reach the desired temperatures, a toggle switch is thrown, which activates the solenoids and unplugs the melting crucibles’ exit holes. Metal flow through the reactor is completed in about 3-4 seconds.

When reheating samples in the thixocasting experiments, a small hole is drilled into the slug to hold the thermocouple. The sample is placed within the furnace using a suspension mechanism that hangs from the overhead beam. The sample is partially remelted at 585°C for about ten minutes, after which it is quenched into a bucket of water located below the furnace.

Metallography of the samples was carried out as follows. Small pieces of the samples were taken from various points in the solidified alloy (bottom, middle, and top positions), and were hot-mounted in bakelite. These were then ground from 320grit up to 4000grit silicon carbide paper. Initial polishing employed a 1µm followed by a 0.3µm alumina suspension, and final polishing was carried out using a 0.04µm colloidal silica suspension. Samples were etched with Keller’s reagent, and optical microscopy was done with MicroGOP software. Data for shape factor and particle size were obtained with AnalySIS software.
5. Results & Discussion

In this section the results from selected liquid mixing experiments are presented. The results are discussed in terms of their microstructural features (including image analysis data), and correlated to the conditions imposed in each experiment. First, results from the thixocasting set of experiments are presented, followed by the rheocasting set. Quantitative correlation between cooling rate through the SSM range and final particle size is then given. Finally, the mechanisms governing SSM structure formation in this process are summarized.

5.1 – Thixocasting route

In the first set of experiments, a thixocasting approach was followed. Here, “as-solidified” samples were reheated to the semi-solid state and quenched. Two variables were investigated in these experiments: superheat of the melts prior to mixing (“T1” experiments) and temperature of the reactor (“T2” experiments).

5.1.1 – Variable: Superheat

Results from three superheat-variable experiments are presented in this section. Table 6 gives the conditions and thermal results of the experiments.
Table 6: Conditions and thermal results for the T1 (superheat-variable) experiments.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$T_{in}$ [°C]</th>
<th>$T_{in}$-$T_L$ (Superheat) [°C]</th>
<th>$T_{out}$ (approx.) [°C]</th>
<th>$T_{reactor}$ [°C]</th>
<th>$dT/dt$ (in crucible) [°C/sec]</th>
<th>Sampling method</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1-2</td>
<td>625</td>
<td>9</td>
<td>611-613</td>
<td>30</td>
<td>-1.10</td>
<td>Air cool; reheat</td>
</tr>
<tr>
<td>T1-3</td>
<td>640</td>
<td>24</td>
<td>613-615</td>
<td>30</td>
<td>-1.08</td>
<td>Air cool; reheat</td>
</tr>
<tr>
<td>T1-4</td>
<td>660</td>
<td>44</td>
<td>615-617</td>
<td>30</td>
<td>-0.85</td>
<td>Air cool; reheat</td>
</tr>
</tbody>
</table>

Figures 26-28 exhibit the representative micrographs from the experiments described above. To the left are the as-solidified structures; at the right are the structures obtained after reheating to 585°C and holding for 10 minutes, followed by immediately quenching into water.
Figure 26: (a) As-solidified and (b) reheated microstructures from experiment T1-2. Residence time of reheated slug in SSM range: 38 minutes.

Figure 27: (a) As-solidified and (b) reheated microstructures from experiment T1-3. Residence time of reheated slug in SSM range: 25 minutes.

Figure 28: (a) As-solidified and (b) reheated microstructures from experiment T1-4. Residence time of reheated slug in SSM range: 18 minutes.
The above three Figures show the effect of raising the superheat of the precursor melts on the resultant microstructures. Each of the above microstructures is highly refined compared to typical as-received ingots. The reheated samples show globular $\alpha$-Al particles distributed in a liquid matrix, with very little entrapped liquid. It is clear that the entrapped liquid in these samples results from coarsening of irregular (i.e. semi-dendritic) particles during reheating. In Figures 26-28 most of the particles have a spherical morphology, but a small portion of them is irregular in shape. Irregularly shaped particles are seen in all results from this study, and their origins are likely related to dendritic growth within the reactor. Although to a limited extent, small dendrites inevitably grow in some parts of the flowing liquid; collisions of these particles may account for the observed shapes. Also evident in the micrographs is an appreciable level of particle agglomeration, which is common characteristic of the structures obtained with the current reactor. It is believed this is a combination of (a) the collisions undergone as the melts flow through the reactor, and (b) grain coalescence during reheating.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Avg. Particle Diameter, As-solidified ($\mu$m)</th>
<th>Avg. Particle Diameter, reheated ($\mu$m)</th>
<th>Avg. Shape Factor, reheated</th>
<th>Number of particles analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1-2</td>
<td>65.2</td>
<td>92.1</td>
<td>0.86</td>
<td>547</td>
</tr>
<tr>
<td>T1-3</td>
<td>76.7</td>
<td>96.8</td>
<td>0.88</td>
<td>409</td>
</tr>
<tr>
<td>T1-4</td>
<td>90.1</td>
<td>101.2</td>
<td>0.87</td>
<td>378</td>
</tr>
</tbody>
</table>

Table 7: Image analysis results for the T1 experiments.
Table 7 summarizes the image analysis results for the micrographs shown. Increasing the superheat clearly results in larger particle size in both the as-solidified and reheated samples. Shape factor data show that increasing superheat does not affect the morphologies of the analyzed particles. Shape factor was determined from the relationship,

\[
\text{Shape Factor} = \frac{4\pi \times \text{Area}}{\text{Perimeter}^2}
\]

A shape factor value of one corresponds to a perfectly spherical particle, whereas values close to zero indicate dendrites or very irregularly shaped particles. In the reheated samples (and slurry samples shown later), only the more spherical particles were analyzed in order to avoid confusion arising from numerical contributions of irregular particles. This was achieved by defining a classification scheme in the analysis program in which particles with very low shape factor values were excluded. Finally, the number of particles analyzed gives an indirect quantification of the degree of particle irregularity in the samples. Although the micrographs chosen may not portray the exact fraction of irregular particles in the entire sample, it is noteworthy that this value decreases for increasing superheat.

In Figure 26, the most uniform as-solidified structure is observed, with the highest level of grain refinement and non-dendritic morphology. Figure 27 exhibits a similar microstructure, but with a larger average particle diameter. There is still a high amount of non-dendritic particles, but a well-globularized SSM structure is obtained upon reheating. Figure 28 has the largest particle size, and shows the highest number of
irregular particles. Even at this high superheat, the particles are for the most part non-dendritic. Despite the higher fraction of irregular particles, the reheated structure indicates a predominantly globular morphology. This may be due to the long residence times of the reheated samples in the SSM range (due to the long time it took for the sample to reach 585°C). Longer residence times lead to coarsening of the particles; therefore initially irregular particles may become more spherical due to the driving force for these particles to reduce surface area. This also explains why for each experiment the particles in the reheated samples are larger than in the as-solidified ones.

It is concluded from this set of experiments that globular structures can be obtained by mixing alloy melts having relatively high superheats. This indicates that the reactor is able to extract very large amounts of heat in a small amount of time. Therefore it is not necessary to have a precursor liquid very close to the liquidus temperature in order to obtain thixotropic structures with this process. Finally, in both the as-solidified and reheated samples, there is a clear trend of (a) increasing particle size for increasing superheat and (b) increasing level of particle irregularity (or tendency to grow dendritically to small degrees) for increasing superheat.

5.1.2 – Variable: Reactor temperature

Table 8 shows the conditions and thermal results for the variable reactor temperature experiments. For T2-4 through T2-6, the superheat was kept the same while the temperature of the reactor was varied. T2-8 had the lowest heat extraction conditions, thus the temperature of the exiting slurry was above the liquidus.
Table 8: Conditions and thermal results for selected T2 (variable reactor temperature) experiments.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>(T_{in} [\degree C])</th>
<th>(T_{in}-T_L [\degree C])</th>
<th>(T_{reactor} [\degree C])</th>
<th>(T_{out} (approx.) [\degree C])</th>
<th>(dT/dt ) (in crucible) [\degree C/sec]</th>
<th>Collection method</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2-4</td>
<td>640</td>
<td>24</td>
<td>130</td>
<td>612.5</td>
<td>-0.81</td>
<td>Air cool; reheat to 585\degree C</td>
</tr>
<tr>
<td>T2-5</td>
<td>640</td>
<td>24</td>
<td>315</td>
<td>614.3</td>
<td>-0.84</td>
<td>Air cool; reheat to 585\degree C</td>
</tr>
<tr>
<td>T2-6</td>
<td>640</td>
<td>24</td>
<td>500</td>
<td>616.4</td>
<td>-0.74</td>
<td>Air cool; reheat to 585\degree C</td>
</tr>
<tr>
<td>T2-8</td>
<td>655</td>
<td>39</td>
<td>315</td>
<td>618.1</td>
<td>-0.75</td>
<td>Air cool; reheat to 585\degree C</td>
</tr>
</tbody>
</table>

The temperature of the reactor was increased in order to decrease its heat extraction capability. The purpose was to vary the processing conditions to give a wide range of particle morphologies, as well as to establish relationships between the variables and the resultant microstructures. In doing so, the limits of the reactor’s heat extraction capability were gauged. Figures 29-32 show the results from the experiments listed above. Again, the as-solidified structures are on the left, with the reheated structures on the right.
Figure 29: (a) As-solidified and (b) reheated microstructures from experiment T2-4. Residence time of reheated slug in SSM range: 24 minutes.

Figure 30: (a) As-solidified and (b) reheated microstructures from experiment T2-5. Residence time of reheated slug in SSM range: 25 minutes.

Figure 31: (a) As-solidified and (b) reheated microstructures from experiment T2-6. Residence time of reheated slug in SSM range: 16 minutes.
The particle size in the as-solidified samples increases slightly from T2-4 to T2-5 due to the lower heat transfer within the reactor. In the reheated samples, it is observed that both experimental conditions lead to highly globular structures of similar particle size. Figure 30(b) shows roughly the same number of irregular particles than in Figure 29(b), and the majority of both structures is globular. In these two experiments, the product slurry exited the reactor at a temperature just below the liquidus temperature of the alloy, resulting in a very low solid fraction, highly fluid slurry. Previous work at MIT with the SSR process [18] suggested that as long as this condition is met (i.e. forming a very low solid fraction rather than cooling the alloy several degrees below the liquidus), then non-dendritic structures result. In other words, all of the particles seen in any given sample must form at or just below the liquidus temperature; therefore it is only necessary to cool the liquid to a one or two degrees below this temperature. The above results show that this reasoning pertains to the CRP as well.
Table 9 lists the image analysis results for the T2 experiments. In the above Table, and throughout this section, the term “average” in relation to shape factor values refers to the mean value taken from the entire data set of all particles analyzed by the classification scheme. It is clear from the micrographs that particle shape irregularity reaches a maximum when the reactor temperature is highest. Numerically, shape factor values are about the same in the first two runs, but change noticeably in experiment T2-6. Also, the number of particles analyzed drops in T2-6, which suggests that more irregular particles were excluded by the classification scheme. Moreover, in T2-6 the presence of non-spherical particles in both the as-solidified and reheated samples is more evident than in the previous experiments. The exiting slurry was just above the liquidus temperature of the alloy, as shown in Table 8, therefore the thermal conditions of the reactor led to a lower level of nucleation. The decrease in nucleation rate led to a larger particle size in T2-6, since grain growth was promoted by the presence of fewer particles. On reheating, a significant amount of liquid was entrapped by the coarsening particles, as seen in Figure 31.
Figure 32 reinforces the reasoning presented above concerning the requirement of a small solid fraction of the slurry upon exit. The exit temperature was 618°C, and these microstructures show the highest degree of dendritic growth. This is because the majority of nuclei formed within the receiving crucible rather than the reactor; therefore there was a lower cooling rate through the alloy’s liquidus temperature. Upon reheating and quenching, the dendrites in the as-solidified structure coarsened, but did not approach the level of sphericity observed in the previous reheated samples.

It is concluded from these experiments that the goal of forming a distinct range of particle morphologies was met by heating the reactor to various temperatures. Particle size increased and shape factor decreased when the reactor was hottest (providing less heat extraction), which suggests less effective heat extraction in the reactor. A higher reactor temperature led to more dendritic morphologies, whereas lower reactor temperatures produced spherical, thixotropic slurry structures. The extent to which the metal is cooled below its liquidus temperature dictates how globular the overall structure becomes.

5.2 – Rheocasting route

In the rheocasting set of experiments, a heated receiving crucible allowed for the direct sampling of semi-solid slurry produced by the CRP. Three different methods of slurry collection were followed. First, slurry was immediately quenched into water without the presence of a receiving crucible; second, several samples of slurry were collected and quenched at various points while cooled slowly through the two-phase
range; and finally, the entire slurry-containing receiving crucible was quenched at one
temperature in the semi-solid temperature range.

5.2.1 – Immediately quenched slurry

In these experiments, the slurry went from the reactor’s exit directly into a large
volume of water. Therefore the sample was immediately quenched and the
microstructure was frozen in place. In the experiment presented below, the temperature
of the precursor melts was 625°C, giving a superheat of about 9°C. The reactor was at
room temperature, as was the water used for quenching. The cooling rate and
temperature of the slurry upon exit was not measured due to the experimental setup, but
the conditions are the same as those in experiment T2-2. Figure 33 shows two
micrographs from this experiment.

Figure 33: Microstructures from experiment R1-1. The sample was immediately
quenched in water upon exit from the reactor.
<table>
<thead>
<tr>
<th>Expt.</th>
<th>Avg. Particle Diameter (µm)</th>
<th>Maximum Particle Diameter (µm)</th>
<th>Minimum Particle Diameter (µm)</th>
<th>Avg. Shape Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1-1</td>
<td>19.7</td>
<td>34</td>
<td>13.6</td>
<td>0.79</td>
</tr>
</tbody>
</table>

The microstructures shown above are much different than those seen in the thixocasting experiments. The primary particles are a great deal smaller, which is to be expected since there is very little time allowed for growth. The fine structure of eutectic phase shows that the cooling rate during quenching was very fast. The smallest particles seen above are less than 15µm in diameter, and the larger ones are less than 40µm, as shown in Table 10. Also, there are many more irregularly shaped particles (as well as some rosettes) observed here than in previous experiments. Two major factors contribute to these morphologies. First, the higher heat transfer undergone within the water bath results in very little particle growth after nucleation. Secondly, the additional convection that is typically experienced by the slurry as it fills the receiving crucible is absent here. Since the slurry is highly fluid on exit, convection from crucible filling may contribute to breaking up of dendrites and spheroidization of the irregular particles. It should be noted that the micrograph containing the dendrites is not representative of the entire sample; rather, they only formed in a particular section of the quenched sample. It is also possible that the dendrites do not form in the reactor, but instead nucleate as the liquid phase is exposed to air in the short distance between the reactor and the water.
When low solid fraction semi-solid slurry is quenched into water, it is expected that large amounts of eutectic be quenched from the liquid phase; therefore the density of the primary particles should be low. However the above Figures dispute this expectation, since a large number of particles is present in the slurry as it exits the reactor. The solid fraction observed in the micrographs, which are from a slurry initially at about 610°C, are much higher than one would expect. This evidence suggests that additional nuclei form during the water quench, and then grow to a very small degree. These nuclei most likely form on particles that were present in the slurry as it exited the reactor.

It is concluded from these experiments that very fine-grained structures are obtained when the slurry is immediately quenched and not collected in a crucible. This finding directly shows that there is a very high density of nuclei in the exiting slurry, which further indicates that copious nucleation takes place in the reactor. Also, the convection/turbulence undergone by the slurry as it fills a receiving crucible may play a role in the mechanisms leading to SSM structure formation in the CRP.

5.2.2 - Slurry quenched at various SSM temperatures

In these experiments, slurry samples were quenched at various temperatures within the SSM range. In the first experiment, a very slow cooling rate though the SSM range occurred due to a high receiving crucible temperature. In the other three experiments, the cooling rate was higher, and was kept nearly constant. In these higher cooling rate experiments, the variable of grain refinement additions was also
investigated. Table 11 lists the conditions and thermal results of the experiments to be presented. For each of these experiments, the reactor was kept at room temperature.

*Table 11: Conditions and thermal results for the R2 (slurry quenching I) experiments.*

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$T_{in}$ [°C]</th>
<th>$T_{out}$ [°C]</th>
<th>$T_{crucible}$ [°C]</th>
<th>$dT/dt$ (in crucible) [°C/sec]</th>
<th>Total residence time in SSM range (min)</th>
<th>Slurry temp. [°C]</th>
<th>Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>R2-2</td>
<td>655</td>
<td>616</td>
<td>585</td>
<td>-0.07</td>
<td>17</td>
<td>605, 597, 590, 585, 575, As-solidified</td>
<td>A356.2 w/ TiB$_2$</td>
</tr>
<tr>
<td>R2-5</td>
<td>625</td>
<td>614</td>
<td>450</td>
<td>-0.22</td>
<td>2.8</td>
<td>610, 600, 590, As-solidified</td>
<td>A356.2 w/ TiB$_2$</td>
</tr>
<tr>
<td>R2-6</td>
<td>625</td>
<td>614</td>
<td>450</td>
<td>-0.23</td>
<td>2.8</td>
<td>610, 600, 590, 580, As-solidified</td>
<td>*SiBloy® w/ AlB$_2$ GR</td>
</tr>
<tr>
<td>R2-7</td>
<td>625</td>
<td>614</td>
<td>450</td>
<td>-0.18</td>
<td>3.6</td>
<td>600, 590, 580, As-solidified</td>
<td>Non-grain-refined A356.2</td>
</tr>
</tbody>
</table>
(a) Slow cooling rate through SSM range

Figure 34 is a collection of micrographs from the first experiment listed in Table 11.

![Micrographs](image)

605°C; t=4.2min  597°C; t=9.6min
590°C; t=14.5min  As-solidified

Figure 34: Microstructural results from experiment R2-2; slurry samples obtained at the specified temperatures and times after slurry collection.

The structures are far superior to those obtained with the thixocasting method. Particle sizes are much smaller using this technique, and size distributions do not vary to an appreciable extent. The presence of dendrites in isolated regions of the samples is an interesting feature, but the majority of these structures are of a globular nature. These
dendrites probably resulted from small volumes of liquid that were deposited into the receptacle just above the liquidus temperature. The presence of even more developed dendrites, as well as several other interesting microstructural features observed throughout the study, is documented in Appendix A.

The above results give direct evidence that the liquid mixing method leads to highly globular semi-solid slurries of fine particle size. Upon entry of these slurries into the heated receptacle, a relatively large amount of time was spent in the SSM range due to the slow cooling rate resulting from a high receptacle temperature. Nonetheless, whatever amount of growth occurred did not result in a significant increase in particle size. The solid fractions suggested by the above Figures, however, are in contradiction with the theoretical values. That is, one would expect to see more liquid phase at a temperature of 605°C. This may be due to the method that the samples were collected and quenched. The sample removal procedure may have resulted in segregation of the solid particles from the liquid phase of the slurry. Also, there may have been slight temperature variations between the location of the thermocouple and the region where slurry was removed (a distance of about 2 inches). Table 12 summarizes the image analysis results for these samples.
Table 12: Image analysis results for experiment R2-2.

<table>
<thead>
<tr>
<th>Slurry temperature (°C)</th>
<th>Avg. Particle Diameter (µm)</th>
<th>Avg. Shape Factor</th>
<th>Number of particles analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>605</td>
<td>68.8</td>
<td>0.83</td>
<td>745</td>
</tr>
<tr>
<td>597</td>
<td>84.2</td>
<td>0.82</td>
<td>377</td>
</tr>
<tr>
<td>590</td>
<td>85.7</td>
<td>0.87</td>
<td>459</td>
</tr>
<tr>
<td>As-solidified</td>
<td>103.2</td>
<td>-</td>
<td>87</td>
</tr>
</tbody>
</table>

It is concluded from these results that by using a heated crucible and collecting slurry during its residence time in the SSM range, even better refined thixotropic structures are observed. The particle sizes are much smaller when compared to the reheated structures of the thixocasting experiments. As seen in Table 12, particle size gradually increases as the slurry is solidified. Average shape factor data do not vary appreciably.

(b) Higher cooling rate with variable grain refinement

Figures 35-37 compare the results from experiments R2-5, R2-6, and R2-7. In R2-5, A356.2 (with TiB₂) was used, whereas SiBloy® was used in R2-6. In R2-7, non-grain-refined A356.2 alloy was used. The purpose of these experiments was twofold: first, to compare the presence of two different kinds of grain refiners to the non-grain-refiner-containing A356.2 alloy; and secondly, to study the effect of a higher cooling rate through the semi-solid temperature range.
Figure 35: Slurries obtained using grain refined A356.2 (above left), SiBloy® (above right), and non-grain refined A356.2 (bottom). Samples quenched at 600°C (1.8 min and 2.0 min after collection, respectively).
Figure 36: Slurries obtained using grain refined A356.2 (above left), SiBloy® (above right), and non-grain refined A356.2 (bottom). Samples quenched at 590°C (2.3min and 2.8min after collection, respectively).
Figure 37: Slurries obtained using grain refined A356.2 (above left), SiBloy® (above right), and non-grain refined A356.2 (bottom). As-solidified structures.

The above three Figures show that the presence of grain refiners in an alloy processed with the CRP only modifies the resultant structures to a small degree. The two types of grain refiners used both lead to a similar particle size. The Figures also clearly indicate that when a non-grain refined alloy is used, the average particle size becomes slightly coarser; however, they still have highly refined structures in comparison to most commercial SSM processes. It should be noted that the cooling rate of the slurry after exiting the reactor in experiment R2-7 was slightly lower than in experiments R2-5 and R2-6, which may have also contributed to this observed trend.
The structures shown above indicate that the level of nucleation obtained with the reactor with *no inoculants present* is sufficient for the formation of equiaxed, non-dendritic structures. They also show that when inoculants are present prior to mixing within the reactor, even finer structures can be produced. Quantitative verification of these statements is presented in Table 13, which shows the general trend of increasing particle size in the three experiments.

*Table 13: Image analysis results for experiments R2-5 through R2-7.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. Particle Diameter (µm)</th>
<th>Avg. Shape Factor</th>
<th>Number of particles analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR A356.2 - 600°C</td>
<td>41.4</td>
<td>0.88</td>
<td>446</td>
</tr>
<tr>
<td>GR A356.2 - 590°C</td>
<td>55.3</td>
<td>0.88</td>
<td>127</td>
</tr>
<tr>
<td>GR A356.2 - As-solidified</td>
<td>66.4</td>
<td>-</td>
<td>203</td>
</tr>
<tr>
<td>GR SiBloy - 600°C</td>
<td>47.6</td>
<td>0.86</td>
<td>305</td>
</tr>
<tr>
<td>GR SiBloy - 590°C</td>
<td>54.2</td>
<td>0.88</td>
<td>241</td>
</tr>
<tr>
<td>GR SiBloy - As-solidified</td>
<td>65.9</td>
<td>-</td>
<td>231</td>
</tr>
<tr>
<td>NGR A356.2 - 600°C</td>
<td>60.5</td>
<td>0.88</td>
<td>561</td>
</tr>
<tr>
<td>NGR A356.2 - 590°C</td>
<td>67.9</td>
<td>0.90</td>
<td>458</td>
</tr>
<tr>
<td>NGR A356.2 - As-solidified</td>
<td>81.0</td>
<td>-</td>
<td>167</td>
</tr>
</tbody>
</table>
When comparing the above results to those shown in Table 12, it becomes clear that the increased cooling rate led to a much finer particle size than in experiment R2-2. Values for shape factor are about the same in all four runs. Figure 38 shows two additional microstructures from experiment SQ9. This sample was quenched at 610°C, corresponding to a low solid fraction.

![Figure 38: R2-5 microstructures at 50X (left) and 200X (right). Sample quenched at 610°C (50 seconds after collection).](image)

The above Figure shows that more nucleation events occur during the slurry quenching technique. Image analysis results of these micrographs are shown below in Table 14. The very small particles nucleated as the scooping utensil (thimble) was used to transfer the sample from the crucible to the water. These nucleation events were likely facilitated by the presence of TiB$_2$ inoculants in the liquid phase of the slurry. Therefore, if this additional nucleation event had not occurred, then the structures would be comprised of the larger particles seen above, combined with quenched eutectic in the regions where the smaller particles are observed. This structure would better reflect the low solid fraction of the slurry at this temperature. The higher magnification
micrograph to the right shows that these secondary $\alpha$-Al particles nucleate on the previously formed particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg. Particle Diameter ($\mu$m)</th>
<th>Avg. Shape Factor</th>
<th>Number of particles analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>R2-5 - 610°C</td>
<td>Large particles (primary nucleation event): 36.1 Small particles (secondary nucleation event): 10.5</td>
<td>0.85</td>
<td>150</td>
</tr>
</tbody>
</table>

It is concluded from these experiments that a higher cooling rate through the two-phase range leads to more refined SSM structures. Also, it is clear that the presence of grain refiners in the alloys used does not significantly affect the particle size and shape of the structures; that is, nucleation rate is not enhanced to an appreciable extent when inoculants are present. The level of equiaxed, non-dendritic growth observed in non-grain-refined A356.2 is high enough to conclude that the reactor design is the major contributor to the observed structures.

### 5.2.3 - Slurry quenched at a single SSM temperature

In these experiments, the entire slurry-containing crucible was quenched into water at a single temperature in the SSM range. The volume of slurry quenched here is much larger than the volumes of “slugs” reheated in the thixocasting set. Two variables were explored in these experiments. First, the effect of a higher cooling rate than the ones in the R2 experiments was investigated. Secondly, instead of using two separate
melts, in experiment R3-4 only one melt was put through the CRP, in order to compare forced convection levels. Table 15 lists the conditions and thermal results for the “R3” experiments.

**Table 15: Conditions and thermal results for selected R3 (slurry quenching II) experiments.**

<table>
<thead>
<tr>
<th>Expt.</th>
<th>T&lt;sub&gt;in&lt;/sub&gt; [°C]</th>
<th>T&lt;sub&gt;out&lt;/sub&gt; [°C]</th>
<th>T&lt;sub&gt;crucible&lt;/sub&gt; [°C]</th>
<th>dT/dt (in crucible) [°C/sec]</th>
<th>Total residence time in SSM range (min)</th>
<th>Slurry temp. [°C]</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>R3-1</td>
<td>625</td>
<td>613</td>
<td>100</td>
<td>-0.70</td>
<td>0.5</td>
<td>588</td>
<td>A356.2 w/ GR</td>
</tr>
<tr>
<td>R3-4</td>
<td>625</td>
<td>614</td>
<td>500</td>
<td>-0.24</td>
<td>1.5</td>
<td>586</td>
<td>One A356.2 melt (w/ GR)</td>
</tr>
<tr>
<td>R3-5</td>
<td>625</td>
<td>614</td>
<td>500</td>
<td>-0.14</td>
<td>3.5</td>
<td>586</td>
<td>Two A356.2 melts (w/ GR)</td>
</tr>
</tbody>
</table>
(a) High cooling rate through SSM range

Among the rheocasting experiments, experiment R3-1 underwent the highest cooling rate through the SSM range; thus its residence time within the two-phase field was the lowest. This explains the small particle size observed below in Figure 39.

Figure 39 shows the most refined microstructure obtained in this study, with primary particles in the range of 30-50\(\mu\)m in diameter. The majority of the particles have a spherical shape. This is an important result because it shows that when a suitable receptacle temperature is chosen, the cooling rate through the two-phase field can be optimized, thus limiting grain growth and forming better SSM structures.
(b) One melt vs. two melts

Experiments R3-4 and R3-5 were carried out in order to see the effect of using only one melt rather than two in the CRP. All other experimental conditions were similar. Figures 40 and 41 show these results.

![Figure 40: Microstructures from experiment R3-4; 25X (left), 50X (right).](image1)

![Figure 41: Microstructures from experiment R3-5; 25X (left), 50X (right).](image2)

Although the processing conditions for R3-4 and R3-5 were similar, the cooling rates (and hence residence times in the SSM range) were not the same, as noted in Table 15. This explains the slightly larger overall particle size in the Figure 40 micrographs, since this sample was within the SSM range for about 2 minutes longer than in R3-5. Also, as mentioned in Table 15, the temperature of the slurries shown above is 586°C,
which corresponds to a solid fraction of about 0.5. The above Figures indeed depict this solid fraction. It should be recalled that in experiment R2-2, the reported slurry temperatures and the observed solid fractions did not seem to match well. The results obtained with this alternate collection technique suggest that this was at least in part due to temperature variations between the thermocouple area and the extracted slurry area. The image analysis results from these three experiments are shown below in Table 16.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Avg. Particle Diameter (µm)</th>
<th>Avg. Shape Factor</th>
<th>Number of particles analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>R3-1</td>
<td>35.2</td>
<td>0.83</td>
<td>155</td>
</tr>
<tr>
<td>R3-4</td>
<td>49.5</td>
<td>0.85</td>
<td>308</td>
</tr>
<tr>
<td>R3-5</td>
<td>63.1</td>
<td>0.75</td>
<td>269</td>
</tr>
</tbody>
</table>

It is evident from the above two Figures that similar SSM structures are obtained when a single melt is used in the CRP. Within the reactor there exists a high number of particle collisions. When one melt is used rather than two, it follows logically that the number of these collisions is reduced (assuming a large number of nuclei form prior to the point at which the melts cross one another). The underlying premise that led to the design of this reactor was that the interaction of two flowing melts would bring about forced convection in order to disperse nuclei, homogenize temperature and composition fields, and suppress dendritic growth. These final experiments show that the level of forced convection that the reactor induces with only one melt is suitable to achieve these goals.
It is concluded from these experiments that the third rheocasting approach, wherein the entire crucible’s contents were quenched, led to globular slurry structures of even finer size. Using a higher cooling rate, particle size was minimized. The use of one melt rather than two in the CRP does not noticeably affect the structures, although there should theoretically be less forced convection. This suggests that the level of forced convection in the reactor using one melt is sufficient for the formation of non-dendritic slurries.

5.3 – Cooling rate vs. particle size

Several image analysis results have been presented in this section, and it is appropriate to compare these numerical data to the cooling rates experienced by the slurries through the two-phase field. Intuitively, slower cooling rates through the SSM temperature range should result in structures having larger particle diameters; the opposite should hold true for higher cooling rates. Figures 42 and 43 show the data from selected rheocasting experiments.
Figure 42: Particle size as a function of cooling rate of the slurry after exiting the reactor. As-solidified structures.

Figure 43: Particle size as a function of cooling rate of the slurry after exiting the reactor. Slurry structures at 590°C.
The above Figures show that higher cooling rates indeed lead to finer particle size in the rheocasting experiments. The results imply that in the rheocasting approach, it is straightforward to determine an optimum cooling rate to yield highly refined and globular structures in the processed slurry. Such an optimum cooling rate, however, while leading to fine particle sizes, must be applied uniformly throughout the bulk of any given sized slurry bath. The data also suggest that in the CRP apparatus, the solid fraction of the processed slurry can be quickly adjusted prior to subsequent forming. From an industrial standpoint, this is highly desirable because uniform slurry structures, which directly impact the uniformity of thixotropic flow in a volume of slurry, can be realized. Furthermore, higher productivity can be achieved because shorter production times can result from faster thermal adjustment of the slurry prior to forming.

5.4 - Discussion of potential mechanisms

The major hypothesis behind this study was that a high nucleation rate combined with turbulence and forced convection leads to (a) copious nucleation of the primary phase, (b) dispersal of nuclei throughout the bulk liquid, and (c) survival of nuclei due to a homogeneous temperature distribution. The results presented here clearly validate this hypothesis. The high level of grain refinement observed in the as-solidified samples can be explained by numerous nucleation events within the reactor. The uniformity of these structures throughout the samples (as well as the degree of particle agglomeration) shows that these nuclei were dispersed effectively by the fluid flow in both the reactor and the receptacle. Survival of the majority of these nuclei “seeds,” though difficult to
verify quantitatively, is strongly suggested by the high nuclei densities seen in the microstructures.

The exact ways in which these nucleation events occur are not easily observed experimentally, but it is theorized that nucleation occurs continuously within the reactor. When liquid fills the channels within the reactor, nucleation occurs at the walls, with consecutive layers of nuclei being swept away by the liquid flowing over them. At the two points in the reactor where the streams cross each other, high levels of convection and particle collisions occur; this was visually confirmed by the similitude experiments. Some of the more irregularly shaped particles likely attained their shapes by colliding with other particles at these junctures. The dispersed particles in the bulk liquid act as sites on which further $\alpha$-Al can grow preferentially. Since a very high number of nuclei is formed, overall particle growth is limited.

During the initial years of SSM research, dendrite breakup by vigorous agitation was the prime mechanism relied upon to form thixotropic structures. However, dendrite breakup is obviously only applicable when there is a dendritic network to begin with. In the CRP, the effects of copious nucleation, nuclei dispersal, and uniform temperature gradients for the most part inhibit dendritic growth, leading to spherical particle morphologies. While the experimental results support this claim, the fundamental mechanisms governing the process have yet to be uncovered. The following paragraphs will discuss the concepts that need to be addressed in the identification of these mechanisms.

At this point an important distinction should be made regarding the sizes and shapes of the particles produced in the CRP. Whereas the sizes of the particles observed
are explained well by nucleation concepts (high density, survival and dispersal of nuclei), the shapes observed can be attributed to fundamental growth concepts. Figures 44 and 45 are schematic representations of two situations in which equiaxed, spherical particles grow in the bulk liquid. Figure 44 describes the solid/liquid interface dynamics for the situation of a single particle growing in a melt without convection.

![Figure 44: Schematic of the solid/liquid interface arising from a single growing equiaxed particle.](image)

The above situation is well described by fundamental solidification concepts [29]. Ahead of the solid/liquid interface exists a boundary layer of solute (not shown in the schematic) that is rejected by the growing α-Al particle. Due to the presence of solute, the local liquidus temperature is not fixed, but rather varies as shown in the schematic (denoted “T_{PD}” since the temperature is dictated by the phase diagram). The temperature gradient in the liquid just ahead of the interface determines the morphology that the particle will take. For example, the temperature distribution might be given by G_{L,1}. Since the temperature given by this gradient is less than the local liquidus temperature, a region of liquid exists (in the area between the two curves) that is “constitutionally undercooled.” If a perturbation develops at the interface, the sub-
liquidus temperature will allow it to grow; thus, a dendritic morphology results. On the other hand, the gradient $G_{L,2}$ gives a temperature distribution that is higher than the local liquidus temperature. Therefore, a perturbation that develops in the interface will not grow, but will melt back due to the hotter liquid. This situation favors the development of a non-dendritic morphology. However, in considering the mechanisms taking place in the CRP, a different situation must be considered, in which several particles nucleate and subsequently grow very close to one another. Furthermore, the presence of forced convection arising from fluid flow must be taken into account. Figure 45 illustrates this situation.

Figure 45 is meant to convey a system in which multiple nuclei are formed and then grow in close proximity to one another. It was shown in the immediate slurry quench experiments that a high density of nuclei is present in the slurry as it exits the reactor. It is thus reasonable to assume that as nucleation occurs, the particles are very close to one another as they grow and are transported by the flowing liquid. Therefore, as shown in the above Figure, the solute boundary layers as well as the solid/liquid
interfaces of neighboring particles may interact with one another as growth occurs. In addition, in a majority of the structures presented several of the particles are in fact in contact with one another. Particle collisions at the onset of growth may also play an important role in the establishment of a non-dendritic growth mode. As a result of these factors, it is more difficult to characterize the local liquidus temperatures and temperature gradients in the liquid ahead of the interface.

The constitutional undercooling argument alone may not be sufficient in explaining the fundamental mechanisms that lead to the observed non-dendritic structures. In the CRP, fluid flow accompanies the early stages of particle growth. Therefore, what needs to be addressed in future work is how fluid flow occurs at the scale of the solid/liquid interface, and whether convection significantly affects the solute boundary layers ahead of the interfaces. One of the objectives in this work was to influence uniform temperature fields in the CRP, in order to mitigate remelting of nuclei. While the high density of particles observed in the structures suggests this is indeed achieved, it is not yet clear how this affects the temperature gradients ahead of the solid/liquid interface. This will also be addressed in subsequent studies.

The above discussion was meant to address the key concerns that must be explored in future investigations of the liquid mixing slurry-making technique. Further work will be carried out in order to conclusively identify and quantify the fundamental mechanisms of non-dendritic growth under forced convection. With this understanding, the Continuous Rheoconversion Process will be optimized, improved, and industrially tested.
6. Conclusions

An apparatus for the controlled mixing of two liquids, the Continuous Rheoconversion Process, has been shown to consistently form non-dendritic semi-solid slurries under a variety of imposed conditions. The process involves the flow of molten aluminum through a static mixing reactor that gives forced convection and copious nucleation of the primary phase. The heat extraction capability of the reactor is high enough to ensure the formation of equiaxed structures even with high superheats in the precursor melts. The combination of forced convection and copious nucleation promotes the formation of small, non-dendritic primary $\alpha$-Al particles.

The first phase of experiments (the thixocasting route) varied the heat transfer conditions within the reactor by changing the melt superheat and reactor temperature, and thus produced a wide range of morphologies. Thixotropic slurry structures were obtained by partially remelting these samples. The second phase of experiments (the rheocasting route) showed that by optimizing the cooling rate through the two-phase field, the microstructural evolution of the produced slurries led to even better-refined structures. Results from the rheocasting approach give direct evidence that the CRP is a suitable precursor device for an industrial slurry-making apparatus. Furthermore, it has been shown that very fine structures can be obtained even when using an alloy containing no grain refining agents. When proper process conditions are chosen, primary particle sizes on the order of 50 microns and shape factor values of 0.90 are attainable. The important conclusions found in this work are summarized below:
• Increasing superheat in the pre-mixed melts leads to larger and more irregular primary particles; highly refined structures are obtained for superheats approaching 45°C.

• Increasing the temperature of the reactor leads to lower heat extraction of the liquid flowing through it; thus, more dendritic morphologies occur at high reactor temperatures.

• Immediately quenched slurry from the reactor shows high nuclei density in the slurry as it exits the reactor. Particle sizes in these samples are the lowest of all rheocasting experiments carried out.

• Slurries quenched at various temperatures in the two-phase field yield highly thixotropic structures, especially when the cooling rate through the SSM range is optimized; grain refining agents only lower particle size by a few microns, suggesting that sufficient nucleation occurs in a non-grain-refined alloy within the reactor.

• The use of a single melt in the CRP yields similar structures as those obtained with two melts, indicating the level of forced convection resulting from one melt is sufficient for suppression of dendritic growth.

The results from this work indicate that the mechanisms at work in this process are related to copious nucleation, dispersal of nuclei in the bulk liquid, and survival of nuclei. Breaking up of dendrites likely occurs in this process, but is not a dominant factor, since dendritic growth only occurs to a limited extent. The results show that this process is highly effective for slurry-making applications, and thus may help in the
development of new rheocasting approaches for semi-solid forming. Future work will address identification of the fundamental mechanisms leading to the observed structures; modeling and optimization of the mixing reactor; rheoconversion of different alloy systems such as hypereutectic aluminum, wrought aluminum, and magnesium; and the proposal of scale-up concepts of the Continuous Rheoconversion Process for industrial applications.
7. References


Appendix A: Micrograph Gallery

In this thesis, the microstructures presented were intended to provide the reader with evidence that the CRP produces thixotropic microstructures under a variety of processing conditions. However, in one experiment (R2-2) some other, very interesting microstructural features were observed that were not pertinent to the topics previously discussed. Therefore, in this section, some of these features will be presented. The morphologies of these samples are noticeably different than many of those shown in the results and discussion section, but it should be stressed that the following micrographs portray isolated regions of the produced slurry, and do not reflect the entirety of the sample.

![Micrograph Gallery](image)

*Figure A-1: Experiment R2-2; $T_{slurry}=597^\circ$C. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth. Note the large size of the dendrite, which likely originated from a small portion of liquid that exited the reactor above its liquidus temperature.*
Figure A-2: Experiment R2-2; $T_{\text{slurry}}=590^\circ\text{C}$. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth.

Figure A-3: Experiment R2-2; $T_{\text{slurry}}=585^\circ\text{C}$. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth. Unusual dendritic morphologies seen throughout the picture at the right.

Figure A-4: Experiment R2-2; $T_{\text{slurry}}=605^\circ\text{C}$. (Left) Typical structure throughout sample; (Right) isolated region of dendritic growth.
Figure A-5: Experiment R2-2; As-solidified structure. (Left) 25X; (Right) 50X. The presence of the observed eutectic “pool” was not seen in any other samples, but it could be a normal phenomenon due to liquid segregation. “Chinese script” phase observed within the pool is likely the compound $\text{Al}_8\text{Mg}_3\text{FeSi}_6$, while the black phase seen above this region is probably $\text{Mg}_2\text{Si}$.

Figure A-6: Experiment R3-2; $T_{\text{shurr}}=585^\circ\text{C}$. (Left) Non-primary phase particle (possibly $\beta$-Si) which seems to be nucleating $\alpha$-Al; (Right) Quenching artifacts near the thermocouple’s stainless steel protection sheath (far right).
The presence of primary silicon particles in the above samples is a strange phenomenon that was not seen in any other samples in this work. Although the temperature reading when this sample was removed and quenched was 575°C, this particular sample was much higher in temperature, probably around 610°C, as indicated by the high fraction of quenched eutectic. Under the high cooling rate experienced by the slurry, it is feasible that small pockets of Si-enriched liquid were able to form β-Si particles. In Figure A-6, the nucleation of α-Al dendrites directly on this particle also suggests that this phase is primary silicon. Figure A-8 shows SEM micrographs of these particles, which were verified by EDX to be primary Si.
Figure A-8: SEM micrographs of the primary Si particles observed in Figure A-7 (top); EDX spectrum of the particle in the right-hand picture, showing only the presence of silicon (bottom).
Figure A-9: Experiment R2-2. (Left) $T_{\text{slurry}}=575^\circ\text{C}$ (Right) $T_{\text{slurry}}=605^\circ\text{C}$. Well-developed dendrites observed.

Figure A-10: (Left) Experiment R3-4, transition zone between globular and dendritic morphologies; $T_{\text{slurry}}=585^\circ\text{C}$ (Right) Experiment R3-5, quenching artifacts adjacent to thermocouple’s stainless steel protection sheath; $T_{\text{slurry}}=585^\circ\text{C}$.
Appendix B: Control experiments – Liquid metal transport tubes

Two experiments were carried out in which the liquid metal flowed from the transport tubes directly into a volume of cold water. In one experiment, the tubes were heated to ten degrees above the melt temperature, as was done in all experiments carried out in this study. In the other, the tubes were kept at room temperature. The purpose was to ascertain that no nucleation took place in along the walls of the tubes en route to the reactor. The temperature of the melts prior to their exit from the melting crucibles was 625°C. The liquid metal was collected in a crucible at room temperature, and allowed to solidify in air. A thermocouple located at the exit of the tube measured the temperature of the liquid before depositing into the water. The alloy used was A356.2 with TiB₂. Table B-1 shows the thermal data for these two experiments.

Table B-1: Conditions and thermal data for the tube control experiments.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$T_{\text{liquid}}$</th>
<th>$T_{\text{tube}}$</th>
<th>$T_{\text{exit}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC-1</td>
<td>625</td>
<td>635</td>
<td>620</td>
</tr>
<tr>
<td>TC-2</td>
<td>625</td>
<td>30</td>
<td>614</td>
</tr>
</tbody>
</table>

As seen in the above Table, when the tube was heated to ten degrees above the temperature of the transported liquid, only about 5 degrees were lost. It is possible that this difference in temperature can be attributed to the cooling effect of the air as the liquid exited the tube. On the other hand, using a cold tube clearly results in more heat being lost in the transported liquid, such that its temperature upon exit is just below the liquidus. Figures B-1 and B-2 show the microstructures of each sample.
The above Figures show that when the transport tube is heated, no nucleation takes place en route to the reactor. The entirety of the structure is comprised of very fine dendrites that nucleate during the water quench. On the other hand, using a tube at room temperature results in a small amount of nucleation in the flowing liquid, as seen in Figure B-2. The larger particles seen here are clearly larger than the surrounding fine dendrites, and thus must have nucleated within the tube. Therefore, it can be concluded that in all of the experiments carried out in this work, no nucleation took place within the heated tubes, but rather occurred within the reactor.