EXPERIMENTAL AND THEORETICAL INVESTIGATION OF ULTRASONIC
CAVITATION PROCESSING OF AL-BASED ALLOYS AND NANOCOMPOSITES

by

YANG XUAN

LAURENTIU NASTAC, COMMITTEE CHAIR
AMBER L. GENAU
LUKE N. BREWER
MARK L. WEAVER
PAUL G. ALLISON

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ABSTRACT

Ultrasonic Treatment (UST) is one of the most promising manufacturing methods to refine the microstructure of casting alloys by transforming the morphology of the grains from dendritic to globular, decreasing the grain size, and modifying the precipitates. The applied temperature and/or temperature range during the ultrasonic and solidification processing are the key parameters that will influence the grain refinement.

In this study, the effects of the temperature and/or temperature range applied during the ultrasonic and solidification processing on the microstructure and nano-particles distribution of the metal-matrix-nano-composites (MMNCs) have been investigated in detail. Aluminum alloy A356 and Al₂O₃/SiC nano-particles are used as the matrix alloy and the reinforcement, respectively. UST is applied during the solidification of the molten alloy. Experimental results indicated that the application of UST during solidification has positive effects on the microstructure of the as-cast ingots. Different UST application temperature/temperature range causes different refinement results. Moreover, the added nanoparticles refined the microstructure of the ingot section that is located adjacent to the immersed cylindrical face of the probe.

Al-Si-Cu alloys have been widely used in the automotive industry. Fe-rich intermetallics are regarded as the most detrimental impurities that diminish the mechanical properties of alloys. In this study, the effect of ultrasound application temperature/temperature range on the pre-dendritic Fe-rich intermetallics (i.e, sludge) has been also investigated. Aluminum alloy A383 is used as the base alloy. Experimental results indicated that by applying UST on the melt highly influences the morphology and distribution of the precipitated Fe-rich intermetallics. Different
UST application temperature/temperature range causes different modification and distribution results of the Fe-rich intermetallics.

To create various temperature gradients in the laboratory scale ingot, an innovative two-zone furnace-ultrasound system has been set up in this study. A numerical model for simulation of the temperature-output power correlation that was validated by using experimental measurements has been built as well. The specific ultrasonic zone that will strongly affect the ingot microstructure has been identified and the ultrasonic attenuation coefficient of aluminum A356 melt has been determined.
DEDICATION

This dissertation is dedicated to my family and my best friends that helped me through the trials and difficulties of creating this study.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\tau$</td>
<td>Material strength</td>
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<tr>
<td>$G$</td>
<td>Shear modulus</td>
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<tr>
<td>$b$</td>
<td>Magnitude of the Burgers vector</td>
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<td>$L$</td>
<td>Distance between pinning points</td>
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<td>$r$</td>
<td>Second phase particle radius</td>
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<td>$\sigma_y$</td>
<td>Yield stress</td>
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<td>$\sigma_0$</td>
<td>Materials constant for the starting stress for dislocation movement</td>
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<td>$K_y$</td>
<td>Strengthening coefficient</td>
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<td>$d$</td>
<td>Grain size</td>
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<tr>
<td>$\alpha$</td>
<td>Ultrasound attenuation coefficient</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
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<tr>
<td>$c$</td>
<td>Ultrasound speed in the liquid</td>
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<tr>
<td>$\eta$</td>
<td>Liquid viscosity</td>
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<tr>
<td>$\lambda_T$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$f$</td>
<td>Ultrasonic frequency</td>
</tr>
<tr>
<td>$c_v$</td>
<td>Specific heats at constant volume</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heats at constant pressure</td>
</tr>
<tr>
<td>$I$</td>
<td>Ultrasonic intensity</td>
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<tr>
<td>$A$</td>
<td>Ultrasonic amplitude</td>
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<tr>
<td>Symbol</td>
<td>Description</td>
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<td>-----------------------------------</td>
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<tr>
<td>γ</td>
<td>Transformed value</td>
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<td>η</td>
<td>Shape parameter</td>
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<td>ε</td>
<td>Shape parameter</td>
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<td>Location parameter</td>
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<td>H</td>
<td>Scale parameter</td>
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<tr>
<td>P</td>
<td>Heat generation</td>
</tr>
<tr>
<td>E</td>
<td>Output power of each coil</td>
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<td>R</td>
<td>Efficiency of the furnace</td>
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<td>S</td>
<td>Thermal radiation</td>
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</table>
ACKNOWLEDGMENTS

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CHAPTER 1 - INTRODUCTION

The Ultrasonic Treatment (UST) can be used to refine the grain structure of light metal alloys. It has been proved that ultrasound applied during the solidification process can induce pressure and temperature oscillations into the melt. Those oscillations increase heterogeneous nucleation and enhance dendrite fragmentation [1-11]. In addition, UST has been reported to modify the precipitated particles in the casting, by reducing segregation and changing their precipitation path.

Aluminum based metal matrix composites (MMCs) are widely used in the automobile and aerospace industries. In this group of materials, micro-size ceramic particles act as matrix reinforcements. The pertinent physical and mechanical properties of Aluminum based MMCs include low density, high specific strength, high wear resistance, high specific stiffness, and low cost [5, 12-17]. However, the ductility of MMCs decreases significantly with the high concentration of ceramic particles. It has been demonstrated that metal matrix nano-composites (MMNCs) that use nano-sized ceramic particles as the matrix reinforcement have similar mechanical properties with MMCs, while maintaining good ductility [18-20]. There are many methods to fabricate MMNCs, such as UST, sol-gel synthesis, laser deposition, high energy milling, ball milling, etc. [12-14, 17, 21-26]. One of the important indicators of the quality of MMNCs is the distribution of the nano-sized ceramic particles in the alloy matrix.

UST is a promising way to fabricate Al-based MMNCs. Ultrasound can induce nonlinear effects such as cavitation and acoustic streaming into the melt, which are very helpful to break and de-agglomerate the nanoparticles in the alloy matrix. Jia et al. [5, 27-32] determined that
Al$_2$O$_3$ and SiC are the optimum types of nanoparticles that can be used as reinforcement in Al-based MMNCs. This is because of their relatively good chemical and thermal stability. The optimum amount of the nanoparticles was determined to be about 1.0 mass %.

In the present study, A356 based MMNCs were fabricated to evaluate the influence of UST on the MMNC matrix. Nanoparticles were added into the molten metal and dispersed by UST. Additionally, UST was applied into the melt during the cooling and solidification process to evaluate the ultrasonic influence on the microstructure formation of castings. Experimental results indicated that the application of UST during solidification plays a key role to refine the casting microstructure of cast alloys. The added nanoparticles refine the microstructure of the ingot region adjacent to the immersed cylindrical face of the UST probe. UST applied temperature/temperature range is an important factor that strongly influence the casting microstructure. The optimum temperature range for applying UST to the melt is ranging from higher than liquidus temperature to lower than solidus temperature of the processed alloys.

Al-Si-Cu alloys have been widely used in automotive industry due to their good castability and high strength to weight ratio [33]. Fe is a common impurity and is regarded as the most detrimental element that lessens the mechanical properties of Al-Si-Cu alloys [34, 35], although the presence of Fe does have a positive effect of preventing die soldering during the permanent mold and high pressure die casting processes [36, 37]. Depending on cooling rate and the amount of Fe and Mn, Fe-rich intermetallics can form as pre-dendritic, pre-eutectic, co-eutectic and post-eutectic phases during the solidification process [38]. The Fe-rich intermetallics that precipitate before the formation of the Al dendritic phase are called pre-dendritic phases. These Fe-rich intermetallics possibly have polyhedral morphology. According to Fabrizi et al. [39], the 3D morphology of pre-dendritic Fe-rich intermetallics corresponds to a regular rhombic
dodecahedron. The pre-dendritic Fe-rich intermetallics can cause severe stress concentration at the matrix/intermetallics interface due to their sharp geometry. The Fe-rich intermetallics that precipitate after the formation of Al dendritic are called post-dendritic phases and the most common phases are α-Fe \((Al_{15}(Fe, Mn)_3Si_2)\) phases with Chinese-script morphology [40] and β-Fe \((Al_3FeSi)\) intermetallics that have long needle-like shape [41]. These post-dendritic Fe-rich phases can block the feeding channels of the inter-dendritic network, resulting in the formation of large amount of porosities and shrinkage in the cast Al alloy, which in turn will significantly decrease its ductility. The platelet β-Fe phases, which are hard and brittle and have a relatively low bonding strength with the matrix Al, are regarded as the most detrimental Fe-rich intermetallics to act as stress raisers that result in the brittleness of Al alloys [42]. Although the term `sludge` for foundrymen is made up of oxides and primary crystals that contain Al, Si, Fe, Mn, Mg and Cr [43, 44]. In this study, the term “sludge” will be used for the pre-dendritic Fe-rich intermetallics phase, `sludge` has been widely accepted to define a specific type of Fe-rich intermetallic, which forms at a relatively high temperature during solidification [45, 46] and the term “α-Fe” and “β-Fe” will be used for the post-dendritic α-Fe phase and β-Fe phase, respectively.

It is important to control the amount and morphology of the Fe-rich intermetallics in Al-Si-Cu alloys to improve their mechanical performance. It has been indicated that a rapid solidification rate or addition of Sr will promote the formation of the more compact, less harmful α-Fe phase, rather than β-Fe intermetallics [47]. Basak et al. [48] introduced a gravitational segregation method to eliminate β-Fe intermetallics in Al-Si alloys. Some other physical segregation techniques, such as magnetic segregation and eddy current segregation, are also used in industry to minimize the content of impurities [49]. In this study, commercial A383 alloys
were selected as experimental samples. Sludge formation temperature has been identified by using Differential Scanning Calorimetry (DSC). According to the DSC results, different UST applying temperature/temperature range has been designed. Experimental results show that applying UST into melt can modify the sludge size or shape. Applying UST in the molten alloy after the sludge precipitation is the most effective way to decrease the sludge size, modify its morphology and disperse sludge uniformly into the melt.

The above-mentioned study indicates that UST application temperature/temperature range is a very important factor of the ultrasonic refinement on the microstructure of cast alloys. Based on this conclusion, a two-zone induction furnace system has been set up in the UA Solicitation and Ultrasonic Processing laboratory. The two-zone system consists of a two-zone generator, a two-zone furnace, a graphite crucible, a chill block and an ultrasonic equipment. The two-zone furnace is an induction furnace with two output coils (a top coil and a bottom coil), which can be power-controlled separately. Providing different output power to the top and the bottom coils can create different temperature gradients in the graphite crucible. Chill block is located at the bottom of the crucible. The temperature data and the simulation results of the furnace output power – melt temperature correlation has been investigated in this research study. The experimental results of cast A356 processed with and without UST show the ultrasonic influence on the cast A356 alloy as well as the ultrasonic influence zone. Based on these experimental results, the ultrasonic attenuation coefficient of the A356 alloy at 18 kHz has been calculated.

The purpose of this study is to research the main several topics mentioned below. The outcome of each research study has also been presented below.
1. The influence of UST during the solidification process on the microstructure formation of as-cast A356 alloy and A356 based MMNCs has been studied. Experimental results demonstrated that nanoparticles in MMNCs have a positive effect on the microstructure refinement. Distribution of nanoparticles (Al₂O₃ and SiC) added into the A356 molten alloy has been evaluated as well.

2. The temperature/temperature range for the application of the UST during melt cooling and solidification has a significant effect on the microstructure refinement of MMNCs. The optimum temperature range has been identified.

3. The formation temperature of the sludge/pre-dendritic Fe-rich intermetallics in an A383 alloy (Al-Si-Cu based alloy) has been identified. It is revealed that the temperature/temperature range for the application of the UST into the melt during sludge precipitation has a significant effect on the sludge morphology, size and distribution. The optimum temperature range has been determined.

4. A novel two-zone furnace system has been set up. A356 melt temperature gradients at different output power has been recorded by using several thermocouples inserted into the melt at various locations. A numerical simulation tool has been developed and validated using the recorded thermocouple measurement data.

5. The ultrasonic influence zone and the ultrasonic attenuation coefficient at 18 kHz of the A356 alloys has been evaluated by using the two-zone furnace system.
CHAPTER 2 - LITERATURE REVIEW

2.1. Metal-Matrix-Composites, Metal-Matrix-Nanocomposites and Aluminum Alloy A356 Based-nanocomposites

Micrometer-size particles are used as reinforcement to fabricate metal-matrix-composites (MMCs) because they can significantly improve composites mechanical properties like hardness and modulus. Aluminum-based matrix composites have been used as structural materials in automotive, aircraft and railway industries. Aero-structural components such as ventral fins and fuel access door covers on F-16 aircraft, rotor blade sleeves and swash plates on Eurocopter EC120 and N4 helicopters are all produced by SiC particulate-reinforced aluminum-based composites [50, 51]. However, the large particles used in MMCs, which size is several micrometers or tens of micrometers, are prone to cracking during loading and leading to premature failure of the composites. Low ductility, low ultimate tensile strength are the main issues of aluminum-based composites that need to be resolved [52-55]. The size of the added particles has a strong effect on the mechanical properties of MMCs. It has been proved that the increase in the particle size decrease the tensile strength and ductility [56]. Jia et al. [57] evaluated the influence of SiC particulate size on the microstructural evolution and mechanical properties of Al-6Ti-6Nb matrix composites. Experimental results showed that the smaller the SiC particle is, the finer composite microstructure is. The in-situ formed intermetallic phase becomes smaller too. An analytical model developed by Zhang et al. [20] predicted that the mechanical properties of metal composites can be enhanced considerably when using ceramic
particles with less than 100nm. This type of metal composite that is reinforced by nanometer-size particles is called metal-matrix-nano-composite (MMNC).

The improvement of mechanical performance of MMNCs could be result from several strengthening mechanism contributions. Orowan strengthening, Hall-Petch strengthening, coefficient of thermal expansion and elastic modulus mismatch [9, 20, 23, 29, 32, 58-60].

The Orowan mechanism consists of the interaction of nanoparticles with dislocations. Dislocations bowing around particle could be expressed as:

\[ \tau = \frac{Gb}{L - 2r} \]  

where \( \tau \) is the material strength, \( G \) is the shear modulus, \( b \) is the magnitude of the Burgers vector, \( L \) is the distance between pinning points, and \( r \) is the second phase particle radius. Under TEM observation, numerous nanoparticles that were engulfed into the metal matrix have been identified [6]. These non-shearable ceramic reinforcement nanoparticles pin the crossing dislocations and promote dislocations bowing around the particles under external load.

The Hall-Petch equation is:

\[ \sigma_y = \sigma_0 + K_y \sqrt{d} \]  

Where \( \sigma_y \) is the yield stress, \( \sigma_0 \) is a materials constant for the starting stress for dislocation movement, \( K_y \) is strengthening coefficient, \( d \) is the grain size. Equation (2) indicates that the smaller grain size is, the larger tensile strength becomes. A theoretically model reveals that the increase of the particle volume fraction and the decrease of the particle diameter lead to a finer grain structure, known as the Zener equation [59].

The mismatch in the coefficient of thermal expansion (CTE) and in the elastic modulus between the nanoparticles and the metal matrix is accommodated during material cooling and straining by formation of geometrically necessary dislocations [23, 32].
The added nanoparticles can be either engulfed into the matrix during the solidification process or be pushed and thus redistribute along the grain boundaries after solidification. Schultz [23] proposed three different types of microstructures of MMNCs can be created depending on the dominant size and degree of nanoparticle clustering, as shown in Fig. 2.1.

Type A is large grains with individual or “small clusters” of nanoparticles within the grain. Strengthening should be high due to Orowan strengthening because of the added nanoparticles into the matrix. Type B is small grains with “medium sized clusters” of nanoparticles located at the grain boundaries. Hardness will be moderate and will dependent on the grain refinement degree (Hall-Petch strengthening). Type C is larger grains with “large clusters” within the grain. Hardness will be low due to the lack of Orowan-type strengthening or grain refinement (Hall-Petch strengthening). It is a promising way to predict the mechanism of MMNCs strengthening.

![Figure 2.1](image)

Figure 2.1. Settlement velocity as a function of particle size [23].
It has been demonstrated by Ma et al. [61] that Al-1.0 vol.% Si$_3$N$_4$ (15 nm) nanocomposite material has a similar tensile strength and significantly higher yield stress compared with that of the Al-15.0 vol.% SiC (3.5 μm) composite material. Work from Lu et al. [62] indicates that nanocomposite Mg-5 wt.% Al-10.3%Ti exhibits higher tensile strength and ductility property than their MMC counterparts, due to the presence of nano-particles in the matrix. Cao et al. [6] reported that by adding 1.5 mass % SiC nanoparticles into Mg-4Zn, the overall mechanical properties including tensile strength, yield strength and ductility of nanocomposites were improved significantly when compared with as cast-Mg-4Zn alloy. The study by Goh et al. [63] indicates that the mechanical properties of Mg-1.3 mass% carbon nanotube (CNT) are improved. However, the addition of more than 1.3 mass% CNT leads to deterioration of mechanical properties, because of the porosity increase caused by clusters of CNT.

Work from Goh et al. [63] shows that one of big challenges facing the widely application of MMNCs is the following: how to avoid clusters of nanoparticles or how to make uniform distribution of nanoparticles within the matrix. Mechanical stirring is a widely used technique in MMCs fabrication. However, it is extremely challenging for the conventional mechanical stirring method to distribute and disperse nanoparticles uniformly into metal melts because of the significantly higher specific surface area of the nanoparticles than that of the micron size particles. After mechanical stirring, nanoparticles tend to agglomerate again or float on liquid surface due to the poor wettability between metal melts and the nanoparticles [16, 64]. In addition, due to the high surface area and the surface dominant characteristics of the nanoparticles, they may be reacted with the metal melt. For example, carbon nanotubes have been reported that they are the suitable reinforcements in aluminum based composites [65, 66].
Formation of brittle and hygroscopic carbides (e.g. Al₄C₃) during the manufacturing process can still happen, these brittle phases deteriorate the mechanical properties of the Al based carbon nanotube nanocomposites [67].

Aluminum alloy A356 (chemical composition in Table 2.1) has good corrosion resistance, good weldability, excellent castability, and it has been widely used in the automobile and aircraft industries. Correspondingly, A356-based nanocomposites have been fabricated and studied in the recent years. Akbari et al. [68] used nano-size TiB₂ as the reinforcement to fabricate A356 based nanocomposites. The processed nanocomposites showed higher ductility and toughness compared with those processed using micron-size particles. Jia et al. [69] indicated a simultaneous increase in the ultimate tensile strength and the elongation for the A356-Al₂O₃ nanocomposites. Zhang et al. [70] fabricated (Al₂O₃+Al₃Zr)/A356 nanocomposites, which was found to have good tensile strength, yield strength and the Brinell Hardness. Hamedan et al. [22] made A356-SiC nanocomposites. Their experimental results showed that the ultimate tensile strength and yield strength of the nanocomposite significantly improved; however, the ductility decreased slightly.

| Table 2.1. Chemical composition of A356 alloys (wt. %) |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Si      | Cu   | Mg    | Zn    | Fe    | Mn    | Ti    | Al    |
| 6.5-7.5 | 0.20 | 0.25~0.45 | 0.10  | 0.20  | 0.10  | 0.20  | Bal.  |

2.2. History and Mechanism of Ultrasound

Ultrasound is an acoustic wave above 20,000 Hertz. The history of using ultrasound on materials science can be traced back to 1878, when Chernov proposed improving cast metals quality by elastic oscillations. The ultrasonic treatment has been used as an environmental-
friendly technique in materials science for purifying, degassing, refinement of metallic materials, and so on [1, 71-77].

Ultrasonic stirring generates nonlinear effects such as acoustic streaming and cavitation into a liquid, as shown in Figure 2.2 [4]. Streaming is affected by the properties of the treated melt, the shape and structure of external boundaries and the momentum loss for overcoming the viscosity of the melt. Ultrasonic streaming increases the transfer of small particles or solid sites in the liquid, equalizes the solute concentration and temperature and help to break the dendritic grains [4, 5, 16, 78]. When ultrasonic cavitation occurs in a melt, the pulsating cavitation bubbles cause the temperature and pressure fluctuations, with temperatures higher than 5,000 K and pressures above 1,000 atm as well as heating and cooling rates near the bubble area above $10^{10}$ K/s. Cavitation is likely to induce heterogeneous nucleation sites into the melt [4, 5, 27, 29].

![Diagram of cavitation and acoustic streaming](image)

Figure 2.2. Schematic diagram of cavitation and acoustic streaming caused by ultrasound [4].
There are several novel fabrication methods of nanocomposites. Azizien et al. [79] successfully fabricated the AZ31 Mg-based nanocomposites reinforced with Al2O3 nanoparticles via Friction Stir Processing (FSP) method. A novel approach by adding Al/nanoparticle ingot into the molten aluminum alloy was performed by Elshalakany et al. [80], Jia et al. [57], Fang et al. [81], and Suryanarayana et al. [82]. They proved that the Mechanical Alloying (MA) is a potential method for achieving very well dispersion of nanoparticles into the nanocomposites. Traditional ball milling and mechanical stirring are not suitable methods to fabricate nanocomposites. Recently, Su et al. [83], Ghahremanian et al. [84], Poirier et al. [85] and Amirkhanlou et al. [86] reported a novel ball milling method to fabricate nanocomposites, which involves mixing reinforcement particles with aluminum powders. It leads to an increase in the wettability of particles with molten aluminum and helps to have homogeneously dispersed nanoparticles into the nanocomposites.

UST is an effective way to spread the nanoparticles in MMNCs. Many studies [12-14, 21-23, 29, 71, 72, 83, 87-93] proved that by introducing UST into the melt for 15 minutes to 60 minutes range breaks the nanoparticle clusters and disperse the nanoparticles uniformly into the melt. The mechanism of UST influence on the nanoparticle dispersion is shown in Figure 2.3. The implosive impact in the melt is generated by the ultrasonic cavitation (Figures 2.3a). It is strong enough to break up the clustered nanoparticles (Figure 2.3b). Meanwhile, the streaming generated by ultrasound helps to disperse nanoparticles uniformly into the melt (Figure 2.3c). The local transient extremely-high temperature (5,000 K) created by cavitation could significantly enhance the wettability between the metal melts and the nanoparticles. Enhanced wettability ensures that the nanoparticles will not re-agglomerate or float on the liquid surface after the UST treatment.
Li et al. [94] introduced a simplified model and suggested that the acoustic cavitation generates adequate pressure that is strong enough to break the SiC nanoparticle clusters in the aluminum melt. Jia et al. [30] simulated the fabrication process of nanocomposites by accounting the turbulent fluid flow, heat transfer, and the complex interaction between the molten alloy and the nanoparticles. Simulation results demonstrated that the nanoparticles can properly be dispersed after 3.0 seconds into the molten aluminum alloy and finally a uniformly dispersed nanoparticle composite could be obtained.

Yang et al. [16] made SiC nanoparticles reinforced composite by using both the mechanical stirring and the UST techniques. The microstructures of each samples are shown in Figure 2.4. Figure 2.4a shows the microstructure of the composites fabricated by conventional mechanical stirring, Figure 2.4b illustrates the microstructure of the nanocomposite fabricated via UST. Comparison of the microstructures revealed that by applying UST during the molten metal processing spread the SiC nanoparticles uniformly into the molten alloys.

Cao et al. [6] reported Mg-4Zn/ 1.5 mass% SiC nanocomposites that were successfully fabricated by UST. Transmission Electron Microscopy (TEM) study indicated that the SiC
nanoparticles were dispersed very well into the matrix and the SiC nanoparticles were bonded well with Mg without forming an intermediate phase. Jia et al. [69] investigated A356 reinforced with 1.0 mass% Al₂O₃/SiC nanoparticles. The experimental results showed a significant improvement in the ductility and tensile strength of the as-cast A356 nanocomposite, which was achieved due to UST treatment.

Lan et al. [64] fabricated SiC nanoparticles reinforced AZ91D-based nanocomposites by UST. Their results showed that the SiC nanoparticles are almost uniformly distributed in the matrix. The micro-hardness of AZ91D + 5 mass% SiC increased by 75% when compared to that of AZ91D. The formation of brittle and hygroscopic carbides (e.g. Al₄C₃) can happen in the aluminum alloy based – CNT reinforced nanocomposites during the manufacturing process [67]. Yan et al. [95] demonstrated that the UST treatment can avoid the formation of Al₄C₃ in the processed nanocomposites.

![SiC nanoparticles distribution of as-cast nanocomposites obtained by different fabrication method [16]: (a) conventional mechanical stirring and (b) UST.](image)

Figure 2.4. SiC nanoparticles distribution of as-cast nanocomposites obtained by different fabrication method [16]: (a) conventional mechanical stirring and (b) UST.

### 2.3. Microstructure Refinement and Modification by UST

It has been proved that by applying UST during the solidification process can refine the metallic alloy microstructure, including decreasing the grain size of the primary phase,
transforming dendritic grains into non-dendritic/globular grain, modifying the morphology of eutectic phase [8, 9, 69, 96-101]. Jian et al. [102] showed that the UST application during the solidification modified the eutectic Si phase in A356 alloys from a coarse acicular plate-like form (no UST) to a finely dispersed rosette-like form (with UST).

Jian et al. [8] reported the mechanisms microstructure refinement using UST during solidification. They specified that refinement of the microstructure can be related to the pressure and the temperature cycle in the melt. Pressure and temperature fluctuations are probably enhancing dendrite fragmentation and increase heterogeneous nucleation in the melt during solidification [8]. UST can produce strong convection and shock waves. Strong convection can promote solute transfer. In addition, convection will cause local temperature and composition variations. Shock waves can induce the breakage of the melting root of the dendrites. Since dendrites usually start melting at their root because of local temperature increase and segregation, UST can promote dendrite fragmentation. On the other hand, when applying UST, melt temperature will change periodically at high frequencies, which means some regions of the melt are superheated and some regions are undercooled. This phenomenon causes increase of the number of nuclei into the melt, which will refine the microstructure [103].

Several factors that could influence the effects of UST during solidification on microstructure refinement have been investigated. It has been reported that [104-107] the ultrasonic grain refinement occurs almost below the radiating face of the UST probe, as shown in Fig. 2.5. UST grain refinement of pure Mg, binary Mg-Al and commercial magnesium alloys has revealed that ultrasonic grain refinement exhibited strong dependence on the solute content of the alloys [100]. The grain size distribution that was evaluated by Qian et al. [107] indicated that grain size increases with increasing distance from the radiator, which can be explained by the
fade of UST convection along the distance from the radiator. When UST probe was inserted into the melt, a solidified layer will form around the probe. However, it has been proved [101] that the formation of the solidified layer around the UST probe has negligible influence on the observed microstructural refinement of the entire ingot.

Figure 2.5. Grain structures of pure magnesium: (a) without UST during solidification and (b) with UST during solidification [107].

Some researchers reported the effects of the application of the UST treatment above the solidus temperature on the formation of the as-cast microstructure [108-112]. Jung et al. [110] applied UST over a temperature range of 750°C-700°C, which is higher than solidus temperature, on near-eutectic commercial Al-Si piston alloys. Results indicated that the UST greatly decreases the size of eutectic cells and tertiary phases, due to the enhanced and prolonged nucleation of each phase by UST. Youn et al. [109] applied UST on hyper-eutectic A390 (17 mass% Si) melt. Characterization results showed that the microstructure of the primary Si phase in A390 alloy is refined and it is more uniform distributed in the Al matrix. The reason of these improvements is that the ultrasound increased the uniformity of chemical compositions in the solute clusters in the
melt, which caused the primary Si phase nucleation enhancement. Promoted nucleation also helped to decrease the grain size and disperse the primary Si phase more uniformly into the melt (Figure 2.6). Youn et al. [109] indicated that the primary α phase of hypo-eutectic A356 (7 mass% Si) does not significantly change when UST was applied at a temperature range of 635°C-743°C. Zhang et al. [112] applied UST at 760°C for 10 minutes for A356 melt, and their experimental results indicated that the long needle shape Si in the eutectic phase were broken into small pieces.

![Figure 2.6. Schematic illustration of the refinement mechanism of primary Si phase in A390 alloy with UST above solidus temperature (top pictures) and without UST (bottom pictures) [109].](image)

Like the propagation phenomenon in water, the amplitude (A) of an ultrasonic wave diminishes or attenuates with distance, when it travels through a liquid metal. Ultrasound attenuation defines the structural refinement to a limited area beyond which the intensity is not strong enough to influence the microstructure. Generally, to achieve cavitation during ultrasonic processing, an intensity of at least 80 Wcm$^{-2}$ is required. This intensity is high enough for structural refinements in lightweight metallic melts [113, 114].

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The Stokes-Kirchhoff relation calculates that the attenuation coefficient of an ultrasonic wave in a liquid theoretically [115-117] as:

\[
\alpha = \frac{2\pi^2}{\rho c^3} \left[ \frac{4}{3} \eta + \lambda_T \left( \frac{1}{c_v} - \frac{1}{c_p} \right) \right] f^2
\]  

(3)

In equation 3, \( \rho \) is the density, \( c \) is the ultrasound speed in the liquid, \( \eta \) is the liquid viscosity, \( \lambda_T \) is the thermal conductivity, \( f \) is the ultrasonic frequency, and \( c_v \) and \( c_p \) are specific heats at constant volume and pressure, respectively. However, it has been found that equation 3 predicts a much smaller coefficient value than those obtained using experimental data for low melting point metals. Qian et al. [114] used an approach to assess the ultrasonic attenuation in molten alloys, and an exponential relationship between the ultrasonic attenuation with propagation distance have been proposed, as shown in equation 4:

\[
I_x = I_o e^{-2\alpha x}
\]  

(4)

where \( I_o \) is the initial ultrasonic intensity or the ultrasonic intensity at the ultrasonic radiator-melt interface, \( \alpha \) is the attenuation coefficient and the ultrasonic intensity \( I \) can be expressed by equation 5

\[
I = \frac{1}{2} \rho c (2\pi f A)^2
\]  

(5)

where \( \rho \) is the liquid density, \( c \) is the sound velocity in the liquid, \( f \) is the ultrasonic frequency and \( A \) is the amplitude of the ultrasound.

2.4. Fe-rich Intermetallics and Aluminum Alloy A383

Al-Si-Cu alloys are being used as replacement materials in automobile engines. Compare with the cast iron components, the benefits of this replacement include resistance to corrosion, good thermal conductivity and moderate costs. Additionally, the total weight of automobile decreases due to the engine material replacement, which will decrease the fuel consumption [118].
It has been demonstrated that by applying the UST during solidification may greatly improve the as-cast aluminum alloy microstructures, by decreasing the primary phase grain size, by transforming dendritic grains into non-dendritic/ globular grains, by modifying the eutectic phase morphology and so on [29, 31, 71]. Jung et al. [119] reported that the tensile properties of a hypereutectic Al-Si alloys containing different Si contents (12, 15 and 18 wt. %) are improved by UST owing to a transformation from dendritic to equiaxed grain morphology. There are some previous research studies that focused on the UST effect on the formation of intermetallics in Al alloys [120-125]. Sha et al. [120] reported that the application of ultrasound leads to improvement of high-temperature tensile strength of hypereutectic Al-20Si-2Cu-1Ni-0.7Fe alloy. By applying UST at different temperatures or temperature ranges during solidification can have various influences on the formation of the microstructure. Zhang et al. [121] evaluated the effects of 60 seconds or 120 seconds ultrasonic treatment on the formation of iron-containing intermetallic compounds in Al-12%Si-2%Fe alloys. The experimental results showed that the application of ultrasound at 720°C contributed to the formation of metastable α-AlSiFe phase rather than the formation of β-AlSiFe phase. As a comparison, applied ultrasound at 610°C could only change the morphology from acicular β-AlSiFe to rod-like β-AlSiFe, without any compositional changes. Puga et al. [122] and Barbosa et al. [123] indicated that by applying UST on Al-9Si-3Cu-0.66Fe melts could refine the morphology of the Fe-rich intermetallic phases, from large needles shape into short and thin particles and suppress the formation of β-phase intermetallics as well. Khalifa et al. [124] reported that the ultrasonic treatment is very effective to convert the long plate-like Fe-rich intermetallic phases to a highly compacted fine polyhedral form in ADC12 die cast alloy (Al-11Si-2Cu-0.78Fe). Also, the critical treatment temperature to affect the Fe-rich intermetallics morphology (596°C-582°C) is higher than the liquidus
temperature of the alloy (i.e., 574°C). Todaro et al. [125] has reported the effect of ultrasonic treatment on macro-segregation and peritectic transformation in Al-19Si-4Fe alloy. The results indicated that the ultrasonic treatment can help reducing macro-segregation and ensure the complete transformation of most of the primary δ-Al3FeSi2 particles into the peritectic β-Al5FeSi phase.

In this study, aluminum alloy A383 has been used to prepare the experimental samples. The chemical composition of A383 alloy has been listed in Table 2.2.

| Table 2.2. Chemical composition of A383 alloys (wt. %) |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Si               | Cu               | Mg               | Zn               | Fe               | Mn               | Cr               | Ni               | Al               |
| 10.5~12          | 1.5~3.0          | ~0.35            | ~2.0             | 0.7~1.3          | ~0.4             | ~0.15            | ~0.3             | Bal.             |
CHAPTER 3 - MICROSTRUCTURE REFINEMENT AND MODIFICATION OF A356-BASED NANO-COMPOSITES VIA UST

3.1 Introduction

A356-based nanocomposites have been fabricated according to the procedure that proposed by Jia et al. [30, 31, 69]. SiC/Al₂O₃ nanoparticles were used as reinforcements. Ultrasound has been applied during the solidification process and the its effect on the microstructure of nanocomposites has been studied. Additionally, nanoparticle influence, UST application temperature influence on the microstructure has been identified.

3.2 Statement of Problem

Most of the literature research is concerned with the impact of UST on nanoparticles distribution during the fabrication process. Applying UST during solidification can modifies the microstructure of casting. However, there is no work focus on the impact of UST on the microstructure of nanocomposites during solidification. Till today, nanocomposites fabrication still has lot of unclear part, evaluating the effect of UST on MMNCs during solidification seems interesting and could have the reference value to the MMNCs production.

It has been proved that UST application temperature/temperature range plays an important role on the matrix microstructure refinement. In this study, the optimum temperature/temperature range to apply UST into nanocomposites during solidification process was determined. The mechanism of MMNCs grain refinement by applying UST at different temperature range was determined based on careful comparisons of as-cast specimen under different conditions.
3.3 Application of UST during Solidification Process of A356-Based Nanocomposites

3.3.1 Experimental Procedure

Aluminum alloy A356 was selected as the metallic matrix. According to previous work done by Jia et al. [30, 32, 69], 1 mass% of ceramic nanoparticles, β-SiC (spherical shape, average diameter is 55 nm) and Al₂O₃ (spherical shape, average diameter is 20 nm), were used in this study as reinforcements to fabricate nanocomposites.

The ultrasonic processing system in this study is illustrated in Figure 3.1. Ultrasonic equipment parameters are shown following: maximum power is 2.4 kW; frequency is 18 kHz, the diameter of the Nb ultrasonic probe is 40 mm and the probe amplitude is around 20 microns. An induction furnace with a capacity of 7 kg was used to melt A356 alloy. Zhang et al. [28] indicated that the nanoparticle injection position will not affect the final distribution of the nanoparticle. In this study, nanoparticles were added into the cavitation area (beneath the ultrasonic probe) during a 15 minutes time-frame.

![Figure 3.1. Schematic representation of the UST and induction furnace equipment.](image)
Five different types of cast samples have been fabricated. The control group experiment is done by melting the A356 alloy in furnace, when melt temperature reach 750°C, turn off the furnace to let the molten metal solidify in the furnace. The UST experiment is done by melting the A356 alloy and turn off the furnace when melt temperature reach 750°C, treating the molten alloy with UST during solidification for about 3 minutes and then let the melt solidify in the furnace. The UST experiments with nanoparticles (Al₂O₃ or SiC) are done by melting the A356 alloy; when temperature reaches 750°C, 1.0 mass % nanoparticles (Al₂O₃ or SiC) assisted by UST were added for about 15 minutes keeping the melt temperature at 750°C, then turn off the furnace; use UST during furnace solidification for 3 minutes then let the melt solidify in the furnace. The fifth sample was obtained as follows: an A356 alloy with 1.0 mass % Al₂O₃ nanoparticles was treated by UST for about 15 minutes after the melt temperature reached 750°C; then the furnace was turned off to let the molten metal solidify inside the furnace. The Nb ultrasonic probe was inserted to about 25 mm beneath the melt surface to perform the UST during solidification. In this case, 3 minutes is the maximum UST application time above which it became difficult to take out the ultrasonic probe.

The cast ingots are cylindrical in shape, ingot diameter is 65 mm and height is 70 mm. The ingots have been split into half, then cut the halves into three parts and labeled as top, middle and bottom, as shown in Figure 3.2. The samples were mechanical ground using #240, #400, #600, #1200 and #2000 grinding papers, respectively. Then they were polished with 1 µm and 0.25 µm diamond polishing agents. The microstructure of the cast samples was characterized in detail via Optical Microscope (OM, Nikon Model Epiphot 200), Scanning Electron Microscope (SEM, JEOL 7000) with an EDS detector (Oxford), and TEM (FEI F20).
3.3.2 Experimental Results and Discussion

Figure 3.3 shows the optical microscopy results in the middle part of the cast ingots. As shown in Figures 3.3 (a) and (b), the A356 samples without UST during solidification have coarser microstructures than the ones with UST. Applying UST during solidification can break up the dendritic structure and thus finer globular grain structure can be obtained. Figures 3.3 (c) and (d) shows the microstructure of A356 with nanoparticles (Al₂O₃ or SiC) with UST during solidification. They have similar microstructures with those shown in Figure 3.3 (b), which means adding nanoparticles will not change the microstructure significantly, and the UST is the main cause of grain refinement. This is confirmed by Figure 3.3 (e), which shows that coarser dendritic grains were obtained in the middle part of the A356 sample reinforced with 1.0 mass% Al₂O₃ processed without UST during solidification. The mechanisms of how UST during solidification refine the microstructure has been explained in Literature Review part.
Figure 3.3. Optical micrographs in the middle part of the cast samples (a) A356 without UST and (b) A356 with UST during solidification and (c) A356 sample reinforced with 1.0 mass% Al₂O₃ and UST during solidification and (d) A356 sample reinforced with 1.0 mass% SiC and UST during solidification and (e) A356 sample reinforced with 1.0 mass% Al₂O₃ without UST during solidification.

The height of the top part of the ingots is about 25 mm, which is the part that is adjacent to the ultrasonic probe. As shown in Figure 3.4 (a), the microstructure of A356 obtained via 3
minutes UST during solidification is dendritic grain, which fits the conclusion of some literature very well [107].

In [107], the authors indicated that the ultrasonic grain refinement occurs almost below the radiating face of the probe, so microstructure of the top part is not as good as the part below the radiating face of the probe. However, all the top part of the samples with the added nanoparticles (Al2O3 or SiC) and UST during solidification have fine globular grains, as shown in Figures 3.4 (b) and (c). However, the microstructure of the top part of the A356 sample reinforced with 1.0 mass% Al2O3 without UST during solidification consists of dendritic grains, which is similar with the microstructure shown in Figure 3.4 (a). Figure 3.4 indicates that the microstructure of the ingot section adjacent to the immersed cylindrical face of the probe can be modified only if both the “addition of nanoparticles” and the “use of UST during solidification” approaches are considered. Applying UST during solidification or adding nanoparticles alone will not change the morphology of the top part microstructure from a dendritic grain to a globular grain. The reason for this can be explained as follows: when applying UST during solidification, the ultrasound intensity of the top part is so weak that it cannot increase the nucleation potential or enhance the dendrite fragmentation (as shown in Figure 3.4 (a)). The added nanoparticles are dispersed very well into the melt, but nanoparticles have no effect on grain refinement (as shown in Figure 3.4 (d)) until UST is applied during solidification. The nanoparticles (Al2O3 or SiC) in the top part will be activated by weak ultrasound, which in turn will increase the nucleation potential during solidification, and consequently to refine the microstructure (as shown in Figures 3.4 (b) and (c)). In addition, since the ultrasound intensity in the middle and bottom parts is strong enough to refine the microstructure (increase nucleation
and enhance dendrite fragmentation), the effect of the UST activated nanoparticles on the microstructure refinement cannot be distinguished.

Figure 3.4. Optical micrographs for the top part of the cast samples (a) A356 with UST during solidification and (b) A356 sample reinforced with 1.0 mass% Al₂O₃ and UST during solidification and (c) A356 sample reinforced with 1.0 mass% SiC and UST during solidification and (d) A356 sample reinforced with 1.0 mass% Al₂O₃ without UST during solidification.

Table 3.1 shows the globular grain size distribution of the measured samples at various locations. The microstructures of the control group and of the top location of the A356 samples obtained via 3 minutes UST during solidification have not been measured because they are not revealing pure globular grain structures.
Table 3.1 Globular grain size distribution of the measured samples at various locations

<table>
<thead>
<tr>
<th>Location</th>
<th>UST</th>
<th>1.0 mass% Al₂O₃+UST</th>
<th>1.0 mass% SiC+UST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>/</td>
<td>119±14.6 μm</td>
<td>120±11.0 μm</td>
</tr>
<tr>
<td>Middle</td>
<td>126±12.7 μm</td>
<td>142±10.7 μm</td>
<td>132±11.3 μm</td>
</tr>
<tr>
<td>Bottom</td>
<td>151±12.9 μm</td>
<td>173±9.6 μm</td>
<td>179±11.4 μm</td>
</tr>
</tbody>
</table>

Table 3.1 shows that for each ingot, the grain size increases from top to bottom and top location has the smallest grain size. The bottom-location globular grain size of A356 samples obtained via 3 minutes UST during solidification is 151 μm, which is 19.8 % larger than that in the middle location. The addition of the Al₂O₃ nanoparticles can refine the top-location microstructure, grain size of the ingot in the middle location is 19.3% larger than that in the top location; the bottom-location globular grain size is 45.3% larger than that in the top location and 21.8% larger than that in the middle location. The addition of the SiC nanoparticles can refine the microstructure in the top location, grain size of the ingot in the middle location is 10.0% larger than that in the top location. The globular grain size in the bottom region is 49.0% larger than that in the top location and 35.6% larger than that in the middle location. Higher the UST intensity, smaller the grain size; basically the grain size differences indicate the UST intensity differences [107]. The results in Table.1 indicate that UST intensity in the current experiment is high enough to refine the entire ingot microstructure and UST intensity decreases with increasing distance from the radiating face. The globular grain size in top part is smaller than that in the middle and bottom parts of the samples with the added nanoparticles (Al₂O₃ or SiC) and UST during solidification because of the faster cooling rates from the top of the furnace, which was exposed to air cooling, and because of its contact with the ultrasonic probe, which was water cooled.
When compare the same location of different samples, A356 samples without nanoparticles have the smallest grain size. Regarding the globular grain size in the middle location, the addition of the Al₂O₃ nanoparticles increases the grain size by 12.7% when comparing with that without nanoparticles; the addition of the SiC nanoparticles increases the grain size by 4.7% when comparing with that without nanoparticles. Regarding the globular grain size in the bottom location, the increase is 14.6% and 18.5%, respectively. The comparison results indicate that by adding the nanoparticles the globular grain size will further increase.

Ceramic nanoparticles Al₂O₃ (spherical shape, average diameter is 20 nm) and β-SiC (spherical shape, average diameter is 55 nm), were used as reinforcements to fabricate nanocomposites in this study.

Figure 3.5 shows the SEM microstructures at high magnification of the A356 sample reinforced with 1.0 mass % Al₂O₃ and UST during solidification. Many nanoparticles can be found in the matrix as highlighted by the red circle in the Figures 3.5 (b) and (c). The nanoparticles have spherical shape and the average size is much smaller than 50 nm, which are similar in size with the nanoparticles added during the processed ingots. The SEM results indicate that the Al₂O₃ nanoparticles are dispersed reasonably well into the A356 matrix. Figure 3.6(a) is the Al₂O₃ nanoparticles used in the experiment. A large nanoparticle cluster with about 1 μm diameter has been found under TEM observation, as shown in Figure 3.6(a). The cluster is formed by lot of nanoparticles with about 50 nm diameter, as shown in the right top section in Figure 3.6(a). Figure 3.6(b) is the nanoparticle found in the as-cast alloy matrix, which has similar morphology and size with the particle shown in Figure 3.6(a). No nanoparticle cluster has been found in the nanocomposite matrix, which indicates that UST help to break the nanoparticle cluster during the fabrication process.
Figure 3.5. SEM results of the sample processed with UST+1.0 mass% Al₂O₃, the red circles highlight the location of the nanoparticles. (a) at X20000 and (b) at X50000 and (c) at X50000.

Figure 3.6. TEM observation. (a) Al₂O₃ nanoparticles used in the experiment (b) Al₂O₃ nanoparticles found in the matrix of nanocomposite.
Figures 3.7 shows the SEM microstructures at high magnification of the A356 sample reinforced with 1.0 mass % SiC and UST during solidification. Unlike the results in the A356 sample obtained by adding Al₂O₃, a significant number of nanoparticles in Figure 3.7 (b) has been found in the grain boundary area. Those nanoparticles have spherical shape and average size is less than 50 nm, which is similar in size with the nanoparticles added during the manufacturing process. Since the particles are in nanometer size, the EDS accuracy is not enough to identify the particle chemical composition, therefore Figure 3.7 (C) only shows the EDS mapping results at relatively low magnification. In the mapping photo, the red color represents C (carbon), the green color represents Al (aluminum). The EDS results indicated that some of C tends to stay in the grain boundary area. By combining the EDS results with the SEM photo, it can be estimated that the SiC nanoparticles are mostly gather around the grain boundary area.

Figure 3.8(a) is the SiC nanoparticles used in the experiment under TEM observation. The added nanoparticles are polygonal shape with size range from 20 nm – 100 nm. Figure 3.8(b) is the nanoparticles found in the as-cast alloy matrix, which has similar morphology and size with the particle shown in Figure 3.8(a). TEM results indicate that there are SiC nanoparticles embed into the matrix.
Figure 3.7. SEM results and EDS mapping photo of the sample processed via UST+1.0 mass% SiC. (a) SEM picture at X500 and (b) SEM picture of red rectangular area in (a) at X50000 and (c) EDS mapping results at X40.

Figure 3.8. TEM observation. (a) SiC nanoparticles used in the experiment (b) SiC nanoparticles found in the matrix of nanocomposite.
3.3.3 Conclusions

The following main conclusions were drawn in this section:

1. This study determined that the application of UST during solidification plays a key role in refining the microstructure of the A356 cast ingots. Without UST processing, dendritic structures were obtained. By using UST during solidification, fine globular grain structures were obtained. The addition of nanoparticles (Al₂O₃ or SiC) is not the main cause for microstructure refinement, however, when UST is applied during solidification, the nanoparticles can modify the microstructure of the ingot part adjacent to the immersed cylindrical face of the UST probe.

2. It was determined that the globular grain size increases with increasing the distance from the radiating face. The addition of nanoparticles (Al₂O₃ or SiC) will slightly increase the grain size.

3. The SEM and TEM results indicated that the added Al₂O₃ and SiC nanoparticles are dispersed reasonably well into the A356 matrix. However, some SiC nanoparticles are gather around the grain boundary area.

3.4 UST Refinement for MMNCs at Different Processing Temperature Range

3.4.1 Experimental Procedure

The experimental system in this study is shown in Figure 3.1. The induction furnace was used to melt the alloy. When the melt temperature reached about 750°C, the ultrasonic probe was inserted to about 50 mm below the melt surface to perform ultrasound cavitation and stirring. 1.0 mass % Al₂O₃ was added into the cavitation area during a 15min time-frame. K-type thermocouples inserted 50 mm beneath the melt surface were used to record the temperature-time evolution during the experiment.
To minimize the effect of the ultrasonic probe cooling effect onto the melt, the ultrasonic probe without turning on the power was preheated by inserting it into the melt at about 750°C. Ultrasonic cavitation processing was controlled by turning on/off the ultrasonic generator power. The temperature-time curve of the melt has been plotted to identify the phase transformation temperature, as shown in Figure 3.9. The liquidus temperature of alloy used in this study is about 614°C (inflexion 1). Inflexion 2 indicates the start of the eutectic phase at about 560°C. Inflexion 3 shows the end of solidification at about 538°C. Figure 3.9 indicates that it takes about 450s for the melt temperature to drop from 614°C to 560°C and about 400 seconds for the melt temperature to drop from 560°C to 538°C. As mentioned in section 3.3.1, it takes about 3 minutes (180 seconds) for temperature of melt drops from 750°C to a low temperature (lower than 614°C). However, according to Figure 3.9, the temperature of melt spent more than 200 seconds drops to 614°C. The time difference between two processes can be explained as follow: experiment in section 3.3.1 did not use the preheated ultrasonic probe, the un-preheated probe will strongly affect melt temperature. This phenomenon was also reported by Qian et al. [101].

Figure 3.9. Temperature – time curve of the A356 alloy.
Based on the temperature-time curve shown in Figure 3.9, three types of experiments were designed: (1) non-treatment UST processing, (2) above-liquidus UST processing and (3) below-liquidus UST processing. In the non-treatment process, after 15 minutes ultrasonic cavitation processing at 750°C, the induction furnace power was shut down to let the melt cooled inside the furnace. Non-treatment UST processing group is the control group in this approach. The second approach, above-liquidus processing, the ultrasonic cavitation was applied into the molten alloy over 650°C-620°C temperature range and the melt cooled inside the furnace. The third experiment was similar with second one but the ultrasonic cavitation processing temperature range was changed to 614°C-600°C. It became difficult to take out the ultrasonic probe when melt temperature lower than 600°C, due to the high proportion of solid phase.

The cast ingots were cylindrical in shape, the ingot diameter is 85 mm and its height is 120 mm. Two small disks were cut from the ingot, as shown in Figure 3.10, and labeled as top and bot, respectively. Disk thickness is 5 mm and distance from the bottom to top and bot disks was 70 mm and 40 mm, respectively. During UST processing, the ultrasonic probe was inserted to about 50 mm below the melt, so the top disk was the section located below the probe, and the bot disk was the section located at 30 mm below the probe. The samples were mechanical ground using #240, #400, #600, #1200 and #2000 grinding papers, respectively. Then they were polished with 1 μm and 0.25 μm diamond polishing agents. The microstructure of the cast samples was characterized in detail via Optical Microscope (Nikon Model Epiphot 200).
3.4.2 Experimental Results and Discussion

Figure 3.11 shows the comparison of obtained microstructures of the nanocomposite of the top disks without the use of ultrasonic cavitation processing during solidification, with ultrasonic cavitation processing at 650°C to 620°C during solidification, and with ultrasonic cavitation processing at 614°C to 600°C during solidification. Figure 3.11(a) shows that when the ultrasonic cavitation processing was not used, the microstructure is dendritic in shape with a large grain size. By applying the ultrasonic cavitation during solidification, regardless of the temperature range, the microstructure is refined significantly as shown in Figures 3.11(b) and (c). The Grain morphologies in Figure 3.11(b) and Figure 3.11(c) are dendritic grain with smaller size and globular grain, respectively. By comparing the microstructures from Figures 3.11(a) and (b), and (c) it can be concluded that for A356-1.0 mass % Al2O3 nanocomposites, UST plays a key role to refine the microstructure during solidification.

Ultrasound will increase the nucleation potential of the melt. This is because when applying ultrasonic cavitation, the temperature and pressure characteristics of the melt will change periodically at high frequencies, which can then locally increase the number of nuclei. In addition, strong convection produced by ultrasonic cavitation can promote diffusion of solute to
increase nucleation, too. Under this circumstance, UST application increases the nucleation in the melt, however, will not break dendritic grain in this alloy. That’s the reason that the microstructure of the alloys obtained by applying UST from 650°C to 620°C (higher than the liquidus temperature 614°C) is dendritic grain in small size. If applying UST at the temperature lower than liquidus temperature. The shock waves produced by ultrasonic cavitation can induce the breakage of the dendrites tips to refine the microstructure. The dendritic fragmentation can strongly change the grain morphology, from dendritic to globular. That’s why the morphology shown in Figure 3.11(c) is globular grain in small size.
Figure 3.11. Optical micrographs of cast samples of the top disks at 50X (a) no ultrasonic cavitation processing during solidification (b) applied ultrasonic cavitation over a range of temperatures from 650°C - 620°C during solidification (c) applied ultrasonic cavitation over a range of temperatures from 614°C - 600°C during solidification.

Figures 3.12 shows the obtained microstructures of the bot disks under three different experimental conditions: (1) without the use of ultrasonic cavitation processing during solidification, (2) with ultrasonic cavitation processing at 650°C to 620°C during solidification, and (3) with ultrasonic cavitation processing at 614°C to 600°C during solidification. Figure 3.12 (a) is similar with Figure 3.11(a), the microstructure is dendritic shape with very large grain size. Figures 3.12 (b) and 3.12 (c) indicate a significant refinement of microstructure when compared with Figure 3.12 (a). The grain morphology was changed from dendritic to globular shape.
Figure 3.12 (b) shows similar microstructure to those shown in Figure 3.11 (b). However, by carefully comparing the microstructures from Figure 3.12 (c) with Figure 3.11 (c), which were taken from the bot and the top sections of the sample processed via ultrasonic cavitation over the range of temperatures from 614°C to 600°C during solidification, it can be concluded that the degree of refinement of the bot disk was not as good as that of the top disk. The reason is explained as follows: when applying UST at 650°C to 620°C during solidification, all cast samples were in the liquid phase, since ultrasonic cavitation intensity was strong enough to influence the bottom section. Thus, the increase in nucleation potential would happen in the whole ingot, which would lead to the similar microstructure shown in Figures 3.11 (b) and 3.12 (b). However, when applying UST at 614°C to 600°C during solidification, the molten melt started to solidify, and by increasing the solid phase the intensity of ultrasonic cavitation and stirring is decreased, and consequently this will diminish the refinement of the microstructure.
Figure 3.12. Optical micrographs of the cast bot disks at 50X (a) no ultrasonic cavitation processing during solidification (b) applied ultrasonic cavitation over a range of temperatures from 650°C-620°C during solidification (c) applied ultrasonic cavitation over a range of temperatures from 614°C-600°C during solidification.

3.4.3 Conclusions

1. Ultrasonic cavitation processing during solidification plays an important role to refine the microstructure of the A356-based nanocomposites. It increases the heterogeneous nucleation in the melt and enhances the dendrite fragmentation.

2. A smaller grain size than that of the control group (without UST application during solidification) was obtained when the ultrasonic cavitation was applied from 650°C-620°C to
an A356 alloy reinforced with Al$_2$O$_3$ nanoparticles during solidification. In this as-cast alloy, the grain size decreases significantly. However, the microstructure is still dendritic.

3. A morphological transition from dendritic grain to globular grain structures was achieved when the ultrasonic cavitation was applied from 614°C-600°C to A356-based nanocomposites during solidification. However, this morphological transition is insignificant at the bottom of the ingot. The reason is that the increasing solid phase amount during solidification is diminishing the intensity of the ultrasonic cavitation.
CHAPTER 4 - MODIFICATION OF FE-RICH INTERMETALLICS IN A383 VIA UST

4.1 Introduction

Aluminum alloy A383 has been used as the matrix metal in this section. The formation temperature of different phases in A383 has been determined. Accordingly, UST has been applied at different temperature/temperature range to evaluate its influence on the formation and morphology of the pre-dendritic Fe-rich intermetallics.

4.2 Statement of Problem

The UST application temperature/temperature range, specifically above/below the precipitation temperature, can strongly affect the UST refinement consequent. Although many researchers [120-125] determined that the UST application helps to refine the morphology of the Fe-rich intermetallic phases, they did not determine the precipitation temperature of the intermetallic in the melt in detail, and the UST application temperature was not based on the precipitation temperature of the intermetallic phase. In this study, UST application temperature/temperature range is carefully designed according to the precipitation temperature of the pre-dendritic Fe-rich intermetallics in A383 alloy.

4.3. Experimental Procedure

Commercial A383 alloys were used to prepare the experimental samples. An induction furnace with 7.7 Kg capacity was used to melt A383 alloy. The ultrasonic system parameters are shown as follows: output power is 2.4 kW, frequency is 18 kHz, diameter of Nb ultrasonic probe is 40 mm and amplitude is 20 microns. K-type thermocouples were used to evaluate the melt temperature during the experiment. The sketch of the system is shown in Figure 4.1. The treated
melt was poured into a steel cup with diameter of 40 mm and height of 35 mm and then the molten melt solidified in air.

Figure 4.1. Sketch of the experimental system.

According to the DSC results, which are discussed in following part, sludge forms in the range of 670°C ~710°C. To investigate the effect of UST on the formation of sludge at different temperatures, UST was applied in three stages: (a) during the entire precipitation process (750°C ~600°C), (b) after the formation of sludge (600°C) and (c) before the formation of sludge (850°C and 750°C), as shown in Table 4.1. For each experiment, the UST probe was preheated in the molten alloy before the turning on the UST power. At the same time, four groups of control experiments without applying UST were conducted as well. The molten alloy was poured out directly to a steel cup immediately after the UST was removed to maximize the cooling rate and thus make sure Fe-rich intermetallics maintain their size and morphology at the temperature applied with UST after the alloy solidified. When the UST was applied into the molten alloy, the temperature was maintained by carefully adjusting the furnace power. For the control groups
without UST, a holding process with the same temperature and duration as in the UST groups was designed.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Molten alloy temperature</th>
<th>Temperature of applying UST</th>
<th>Time of applying UST</th>
<th>Pouring Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>750°C</td>
<td>---</td>
<td>---</td>
<td>600°C</td>
</tr>
<tr>
<td>2</td>
<td>750°C</td>
<td>600°C</td>
<td>15 min</td>
<td>600°C</td>
</tr>
<tr>
<td>3</td>
<td>750°C</td>
<td>---</td>
<td>15 min</td>
<td>750°C</td>
</tr>
<tr>
<td>4</td>
<td>750°C</td>
<td>750°C</td>
<td>15 min</td>
<td>750°C</td>
</tr>
<tr>
<td>5</td>
<td>850°C</td>
<td>---</td>
<td>15 min</td>
<td>850°C</td>
</tr>
<tr>
<td>6</td>
<td>850°C</td>
<td>850°C</td>
<td>15 min</td>
<td>850°C</td>
</tr>
<tr>
<td>7</td>
<td>750°C</td>
<td>750~600°C</td>
<td>4 min</td>
<td>600°C</td>
</tr>
</tbody>
</table>

Metallographic specimens were all taken from the same location, which is the center of the cast ingot. The samples were mechanical ground using #240, #400, #600 and #2000 grinding papers, respectively, and then they were polished with 3 μm and 1 μm diamond polishing agents. The microstructure of the cast samples was characterized in detail via Optical Microscope (OM, Nikon Model Epiphot 200) and SEM (JEOL 7000) with an EDS detector (Oxford). To get the size of the sludge, five different fields under 100X were analyzed for each sample, and at least 200 sludge grains were measured. DSC (Setaram Setsys Evolution TGA-DSC/DTA) was also performed to analyze the precipitation temperature of the sludge as a function of cooling rate. The samples used for DSC analysis, with a mass of 40 mg, were melted under a protective Ar gas flow of 50 mL/min. The sample was heated to 850°C with a heating rate of 10 K/min, then solidified with different cooling rates (5 K/min, 10 K/min, 20 K/min and 50 K/min). The reference for DSC analysis was an alumina crucible.
4.4. Results

4.4.1 DSC Results

It is shown in Figure 4.2 that there are four exothermic peaks during the solidification process of A383 alloys. The peaks 1 to 4 correspond to the formation of the sludge, $\alpha$-Al dendrites, Al-Si eutectic and Al-Cu phases, respectively. The full analysis of the DSC results is summarized in Table 4.2. It is clear that the sludge forms at a relatively high temperature (669°C~704°C) that is before the formation of the primary $\alpha$-Al (562°C~569°C) and of the eutectic Si phases (544°C~559°C). Also, the precipitation temperatures of both the sludge and the Al-Si eutectic decrease as the cooling rate increases. In contrast, the precipitation temperature of the Al-Cu phase increases as the cooling rate increases. It is notable that the precipitation temperature of the sludge is much more sensitive to cooling rate. The peak corresponding to the formation of primary $\alpha$-Al (peak 2) reduces and finally disappears with increasing cooling rate.
Figure 4.2. DSC solidification curves of A383 alloys with cooling rates of 5 K/min, 10 K/min, 20 K/min and 50 K/min, respectively. Note that no "peak 2" was observed for the 50 K/min cooling rate.

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>1(Sludge)/ ºC</th>
<th>2(Al-dendrite)/ ºC</th>
<th>3(Al-Si eutectic)/ ºC</th>
<th>4(Al-Cu phase)/ ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 K/min</td>
<td>680–715 (704)</td>
<td>563</td>
<td>559</td>
<td>482–500 (491)</td>
</tr>
<tr>
<td>10 K/min</td>
<td>678–713 (696)</td>
<td>562</td>
<td>555</td>
<td>480–504 (494)</td>
</tr>
<tr>
<td>20 K/min</td>
<td>667–710 (692)</td>
<td>569</td>
<td>549</td>
<td>492–512 (507)</td>
</tr>
<tr>
<td>50 K/min</td>
<td>642–691 (669)</td>
<td>---</td>
<td>544</td>
<td>499–513 (508)</td>
</tr>
</tbody>
</table>

*The value in bracket is the position of exothermic peak.
4.4.2 The Analysis of Fe-rich Intermetallics

Several different morphologies of the sludge/α-Fe phase were observed. The prevalence of each morphological type depended upon the solidification conditions. For high melt temperatures without UST (750°C and 850°C), large, dendritic sludge phases were observed (Figure 4.3 (a)). Large, polygonal sludge (Figure 4.3 (b)) and small island-like sludge (Figure 4.3 (c)) were observed for a range of solidification temperatures and appeared both with and without UST. The α-Fe phase with Chinese-script morphology was observed for all conditions with a pouring temperature higher than 600°C (experiments 3-5 in Table 4.1) (Figure 4.3 (d)). In addition, the α-Fe phase was not observed for experiment 6 which had a melt temperature of 850°C, a pouring temperature of 850°C and UST applied at 850°C. In many cases, an Cu-rich phase was observed along the interfaces between the primary α-Al phase and the sludge. The distribution of different chemical elements in Figure 4.3 (a) was investigated through EDS mapping and the results are shown in Figure 4.4. These x-ray maps indicated that the sludge was enriched with Fe, Mn and Cr. The measured compositions of α-Fe and sludge are shown in Table 4.3. The results show that the sludge contains more Mn and Cr than the α-Fe phase and a lower ratio of Fe/Mn. The concentrations of Si in α-Fe and sludge are similar.
Figure 4.3. SEM images of different types of Fe-rich intermetallics: (a) large needle-like sludge, (b) large blocky sludge, (c) small island-like sludge (d) α-Fe with Chinese-script feature.
4.4.3 Effect of UST on the Formation of Sludge

The use of UST during solidification refined the size and shape of sludge particles, but was particularly effective at lower application temperatures. Figure 4.5 shows the effect of UST on the formation of sludge when it is applied at 600°C for 15 minutes. It is clear that the sludge has a homogeneous distribution as well as a small size with polyhedral morphology when UST is applied at 600°C, as indicated in Figure 4.5 (b). UST applied at 600°C reduced the size of the sludge particles (Figure 4.5 (b)) as compared with the control sample without UST (Figure 4.5 (a)). Application of UST had less impact on the formation of sludge when applied at

Table 4.3. Quantitative compositional measurements of Fe-rich intermetallics (wt. %)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Fe/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge</td>
<td>59.4±0.1</td>
<td>9.9±0.2</td>
<td>18.1±0.2</td>
<td>8.7±0.1</td>
<td>3.7±0.2</td>
<td>2.1</td>
</tr>
<tr>
<td>α-Fe</td>
<td>61.8±0.1</td>
<td>9.5±0.1</td>
<td>21.8±0.3</td>
<td>5.8±0.5</td>
<td>1.1±0.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Figure 4.4. EDS mapping of needle-like sludge.
temperatures higher than the sludge precipitation temperature (700°C) (Figure 4.6). Large sludge particles (>400 μm) with long, platelet-like morphology were observed in the alloy that was cast at 850°C without UST (Figure 4.6 (a)). Some α-Fe phases in Chinese-script shape were also found in this alloy, as shown in Figure 4.6 (b). The microstructure of the sample that was obtained with UST at 850°C for 15 minutes is shown in Figures 4.6 (c) and (d). It indicates that the sludge and the α-Fe are still present in the Al matrix and there is some relative variation in both the size and the morphology of these two Fe-rich intermetallics, when compared to the samples without UST. However, for the sample that was cast at 750°C without UST, the majority of observed, Fe-rich intermetallics are α-Fe with Chinese-script morphology, as shown in Figure 4.6 (f). A small amount of the sludge is observed only at the bottom of the casting and its sludge exhibited polyhedral morphology, as shown in Figure 4.6 (e). Figures 4.6 (g) and (h) illustrate the microstructures of the alloy obtained with UST applied at 750°C for 15 minutes. In the alloy processed with UST, the majority Fe-rich phases are sludge rather than α-Fe intermetallics.

Figure 4.5. Typical optical images of alloys cast at 600°C (a) without UST (b) with UST at 600°C for 15 minutes.
Figure 4.6. Typical optical microstructures of alloys with UST applied at high temperature. (a) and (b) 850°C without UST, (c) and (d) 850°C with UST for 15 minutes, (e) and (f) 750°C without UST, (g) and (h) 750°C with UST for 15 minutes.

Figure 4.7 shows the effect of UST on the formation of sludge when it is applied from 750°C ~600°C. Sludge with branch shape has been observed in the sample that was processed without UST, as indicated by arrow in Figure 4.7 (a). However, when UST was applied from 750°C~600°C, the large branch shape sludge disappears and all the sludge exist in small island-like or polyhedral shape, as shown in Figure 4.7 (b). Consequently, the application of UST from 750°C~600°C assists to modify the sludge morphology from branch shape to island-like shape.
4.4.4 Quantitative Microstructural Analysis

Application of UST to the melt decreases the sludge size and variability significantly. The average sludge particle size (area of particle) and sludge roundness (value of unity is a circle) of each sample were evaluated. Each value was obtained by measuring more than one hundred sludge particles for each sample (see Table 4.4). The average sludge particle size processed with 15 minutes UST at 600°C and cast at 600°C (472 µm² ± 378 µm²) is 60% smaller than the sample cast at 600°C without UST (1,121 µm² ± 1,144 µm²). One should note that not only does the average sludge particle size decrease, but the variability of the sludge particle size decreases. The sludge particle size of the sample that was processed with 15 minutes UST at 750°C and cast at 750°C (1,455 µm² ± 1,305 µm²) is 62% smaller than the area of samples cast at 750°C without UST (3,839 µm² ± 3,826 µm²). The sludge particle size of the sample that was processed with 15 minutes UST at 850°C and cast at 850°C (1,916 µm² ± 1,763 µm²) is 72.9% smaller than the particle size of the sample cast at 850°C without UST (7,073 µm² ± 7,000 µm²). The overall comparison of all results (Table 4.4) indicate that applying the UST to the melt decreases the sludge size significantly.
Table 4.4. The average sludge particle size for each sample

<table>
<thead>
<tr>
<th>Sludge area (µm²)</th>
<th>600°C</th>
<th>750°C</th>
<th>850°C</th>
<th>750-600°C with UST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without UST</td>
<td>1,121 ± 1,144</td>
<td>3,839 ± 3,826</td>
<td>7,073 ± 6,862</td>
<td>-</td>
</tr>
<tr>
<td>With UST</td>
<td>472 ± 378</td>
<td>1,455 ± 1,305</td>
<td>1,916 ± 1,763</td>
<td>991 ± 830</td>
</tr>
</tbody>
</table>

Figure 4.8 shows the sludge roundness distribution of the samples processed under different process conditions. It can be seen from Figure 4.8 that the sludge roundness value slightly increased when the melt was treated by UST at 600°C/750°C, compared with that without UST treatment. The sludge roundness value did not significantly change when UST was applied at 850°C. However, when UST was applied between 750°C-600°C during solidification, the roundness increased considerably.

Figure 4.8. The sludge roundness distribution of the processed samples.

Figure 4.9 presents the sludge particle size distribution of the samples with/without 15 minutes UST and cast at 600°C. It can be seen from Figure 4.9 that all sludge particle sizes of
the sample processed with 15min UST at 600℃ are smaller than 2000 µm² and only few sludge particle sizes are larger than 1,000 µm², while a significant number of sludge particle size in the sample cast at 600℃ without UST are larger than 2,000 µm². Figure 4.10 presents the sludge-equivalent spherical diameter of samples processed with/without 15 minutes UST and cast at 600℃. The results shown in Figure 4.10 indicate that the 15 minutes UST at 600℃ decreases the sludge size.

Figure 4.11 shows the sludge particle size distribution of the samples with/without 15 minutes UST and cast at 750℃. The distribution of sludge particle size of the sample that was treated by UST for 15 minutes and cast at 750℃ is heavily weighted for particle sizes below 4,000 µm². The sludge particle size of the sample cast at 750℃ without UST vary between about 100 µm² and 16,000 µm². Figure 4.12 presents the sludge-equivalent spherical diameter of samples processed with/without 15 minutes UST and cast at 750℃. The results shown in Figure 4.12 indicate that 15 minutes UST at 750℃ decreases the sludge size.

Figure 4.13 illustrates the sludge particle size distribution of the samples processed with/without 15 minutes UST at 850℃. The small graph in Figure 4.13 shows the detail of the sludge area distribution of these samples. Most of the sludge areas of the sample processed without UST and cast at 850℃ vary between about 100 µm² and 20,000 µm². Few of them are in the range of 20,000 µm² to 70,000 µm². When applied UST, almost all sludge is smaller than 10,000 µm². Figure 4.14 presents the sludge-equivalent spherical diameter of samples processed with/without 15 minutes UST at 850℃. The results shown in Figure 4.14 indicate that 15 minutes UST at 850℃ decreases the sludge particle size and prevent the abnormal sludge formation.
Figure 4.9. The sludge particle size distribution of samples processed with/without 15 minutes UST at 600°C.

Figure 4.10. The sludge equivalent spherical diameter of samples processed with/without 15 minutes UST at 600°C.
Figure 4.11. The sludge particle size distribution of samples processed with/without 15 minutes UST at 750°C.

Figure 4.12. The sludge equivalent spherical diameter of samples processed with/without 15 minutes UST at 750°C.
4.5. Discussion

4.5.1 Thermal Analysis of A383 Alloy during Solidification

The effect of cooling rate on the precipitation of different phases is investigated and the result is shown in Figure 4.15. The precipitation temperature of the sludge drops from 704°C to 669°C as the cooling rate increases from 5 K/min to 50 K/min, which is consistent with the conclusions of Ferraro et al. [126]. It is also observed by Ferraro that the increasing cooling rate
will increase the amount of sludge by promoting the nucleation rate. Because of the high precipitation temperature of the sludge, it can grow unimpeded by other solid phases and therefore can achieve a large size. The Si concentration of A383 used for this work is 10.5~12 mass%, which is very close to the eutectic point (12.6 mass%), so the peaks of primary Al and Al-Si eutectic are overlapped to such an extent that they are merged in the thermal traces, as shown in Figure 4.2. However, the precipitation temperature of Cu-rich phases increases as the cooling rate increases. The Cu-rich phases typically form together with the Fe-rich intermetallics [127]. Therefore, increasing cooling rate may increase the nucleation frequency of the sludge and thus more nucleation sites for Cu-rich phase are generated. As a result, the undercooling for the formation of the Cu-rich phase is decreasing and the precipitation temperature of the Cu-rich phases tends to increase.

![Figure 4.15. The precipitation temperature of the alloy phases as a function of cooling rate.](image)
4.5.2 Effect of UST on the Formation of Sludge at Various Temperatures

Table 4.4 and Figure 4.9 indicate that applying UST for 15 minutes at 600°C significantly decreases the sludge size and makes the sludge area value distribution more uniform. In addition, as shown in Figure 4.5, the morphology of sludge transforms from branched to a polyhedral shape, and the roundness is slightly increased when applying UST. Those changes from applying UST are explained as follows: The sludge already formed in the Al melt at 600°C The cavitation generated by ultrasonic waves will break the dendritically shaped sludge into pieces, thus decreasing the sludge size, and changing the sludge morphology to polyhedral shape. In addition, the acoustic streaming generated by UST will generate melt agitation, which in turn will help to distribute the sludge phase uniformly into the molten alloy [29, 103, 128]. These uniformly distributed, scattered small sludge particles start to grow at 600°C, thereby consuming elemental Fe in the melt, which inhibits the precipitation of the α-Fe.

Figures 4.11-4.14 indicate that application of UST in the sample at 750°C or 850°C decreases the sludge size, achieves uniform sludge area distributions and effectively inhibits the formation of abnormally large sludge particles. According to the DSC results (as shown in Table. 4.1), 750°C and 850°C are higher than the sludge formation temperature. By comparing the sludge areas in Figures 4.11 and 4.13, it can be observed that by applying UST at temperatures higher than the sludge precipitation temperature can be very effective in reducing the sludge size. The reason that UST treated samples have a smaller sludge particle size is that ultrasound can enhance the wetting of inclusions with melt and deagglomerates the inclusions, which will consequently increase the potential nuclei in the melt, thus decreasing the sludge size [129, 130]. However, when applying UST at temperatures higher than the sludge precipitation temperature, there is no sludge fragmentation during growth, resulting in a sludge with branch shape, which...
was found in the samples processed with 15 minutes UST at 750°C and 850°C. Additionally, the sludge area of the sample that was processed with 15 minutes UST at 750°C and cast at 750°C is 24.1% smaller than that of the sample processed with 15 minutes UST at 850°C and cast at 850°C, which indicates the closer the UST processing temperature to the sludge precipitation temperature, the more significant the UST sludge grain refinement effect.

Table 4.4 indicates that when the sample was treated by UST from 750°C to 600°C in the furnace during cooling and cast at 600°C, the average sludge size of the sample was 991 µm² ± 830 µm², 11.6% smaller than the sample without UST cast at 600°C; however, it is 109.9% larger than the sample that was processed with 15 minutes UST at 600°C. The sludge area distribution of different samples treated by ultrasound has been shown in Figure 4.16. Figure 4.16 indicates that in comparing the three different treatments, the application of UST for 15 minutes at 600°C is the most efficient treatment to modify the sludge size, which was smaller than 4,000 µm². Applying UST from 750°C to 600°C makes the distribution of sludge size uniform, but it is not as efficient as the UST treatment for 15 minutes at 600°C. However, the sample that was treated by UST from 750°C to 600°C has the highest sludge roundness value when compared with the other samples, as shown in Figure 4.8. This means that it is the most efficient UST treatment to refine the sludge shape. The UST applied from 750°C to 600°C on the molten alloy influences the sludge nucleation and growth: first, the ultrasonic energy homogenizes the Fe element into the melt when the melt temperature was varied from 750°C to the sludge precipitation temperature, the UST cavitation activates the melt inclusions as potential nuclei, and thus to increase the sludge nucleation potential. The increase in the sludge nucleation intensity may inhibit the formation of unusually large sludge. In addition, cavitation generated by UST breaks the branch-shape sludge into pieces cast. However, the ultrasonic treatment time from 750°C to 600°C was
only 4min, melt agitation generated by UST acoustic streaming did not have enough time to
distribute the sludge uniformly in the melt, and this is the main reason for the sludge aggregation,
as shown in Figure 4.4(b).

![Figure 4.16. The sludge particle size distribution of samples with UST at 600°C, 750°C and 750°C-600°C.](image)

4.5.3 Data Statistical Analysis

A statistical analysis was performed to determine the sludge size distribution of all
processed samples by using the software Minitab™ (see Appendix A).

Several statistical analysis approaches were evaluated. Unbounded System (SU) Johnson
transformation (Equation 6) was identified as the best option that transforms raw data into a
standard normal data [131, 132]:

\[ y = \gamma + \eta \text{Sinh}^{-1}\left(\frac{x - \varepsilon}{\lambda}\right) \quad \text{with} \quad \text{Sinh}^{-1}(z) = \ln(z + \sqrt{1 + z^2}), \]  

(6)

where \( y \) is the transformed value, \( \gamma \) and \( \eta \) are shape parameters, \( \varepsilon \) is the location parameter and \( \lambda \)
is the scale parameter. The equation parameters can be calculated by using the equations for the
parameter estimates that was introduced by Slifker et al. [133].
The P-value is the level of marginal significance within a statistical hypothesis test representing the probability of the occurrence of a given event. A small P-value (typically ≤ 0.05) indicates strong evidence against the null hypothesis, therefore rejects the null hypothesis. A large P-value (>0.05) means weak evidence against the null hypothesis and fail to reject the null hypothesis. In this study, P-value of each sample has been listed in Table 4.5. It can be seen from Table 6 that the P-value of the sample cast at 600°C without UST is the only one that is lower than 0.05, which indicates that the sample cast at 600°C without UST rejects normal distribution.

The analysis results and the transformed data of all samples are plotted in Figure 4.17. In Figure 4.17, the histogram and solid-line curve in each picture represent the real data after Johnson transformation and the related normal distribution, respectively. Figure 4.17 indicates that all samples except the sample cast at 600°C without UST meet the normal distribution. However, the sludge size distribution of the sample cast at 600°C without UST has more variation.

<table>
<thead>
<tr>
<th>P-value</th>
<th>600°C</th>
<th>750°C</th>
<th>850°C</th>
<th>750°C-600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without UST</td>
<td>≤ 0.05</td>
<td>0.549</td>
<td>0.742</td>
<td></td>
</tr>
<tr>
<td>With UST</td>
<td>0.553</td>
<td>0.976</td>
<td>0.836</td>
<td>0.531</td>
</tr>
</tbody>
</table>
Figure 4.17. Statistical evaluation of all processed samples.
4.6. Conclusions

A quantitative analysis regarding the effect of UST on the morphology and size of sludge under different solidification conditions has been performed. The results indicate the following: The sludge will precipitate before the formation of the primary Al matrix phases during the solidification process and the precipitation temperature of the sludge will decrease with increased cooling rate.

The application of UST after the precipitation of sludge (600°C) reduces the size of the sludge modifies its morphology from a branched shape to a polyhedral shape. In addition, the acoustic streaming generated by UST will generate melt agitation, which in turn will help to distribute the sludge phase more uniformly in the molten alloy.

Application of UST before the sludge precipitation (750°C or 850°C) helps to reduce the sludge phase size due to the increase in the nucleation intensity of the sludge. However, the sludge still has a branched shape.

Application of UST during the solidification process (750 °C ~600°C) reduces the sludge phase size and breaks large sludge particles into small island-like pieces. However, these sludge phase particles still tend to agglomerate since UST stirring time currently used is insufficient.

In summary, applying UST in the molten alloy is an effective method to refine sludge in the A383 alloy. UST is most effectively applied to the molten alloy at lower temperatures (600°C) after the precipitation of the sludge phase.
CHAPTER 5 - TWO-ZONE FURNACE SYSTEM SET UP

5.1. Introduction

A new equipment consisting of a two-zone furnace and an ultrasound system has been set up in the Ultrasonic and Solidification Processing Laboratory. The two-zone furnace is an induction furnace with two separate coils (a top coil and a bottom coil). By controlling both the top and the bottom coil output power, the furnace can create different temperature gradients in different parts of the crucible. The crucible is opened at both ends and it is made of graphite. A water-cooled chill block has been designed and then applied at the bottom of the crucible. Ultrasound can be applied at the top of crucible.

Conclusions in previous sections indicate that applying UST at mushy zone (temperature higher than solidus temperature but lower than liquidus temperature) can decrease the matrix grain size and modify the grain from dendritic morphology into globular morphology. When insert an ultrasonic probe into a mushy zone during the solidification process, the challenge must be faced is that it becomes more and more difficult to take out the probe from the melt as the temperature decreases.

The two-zone furnace system is a promising way to overcome this challenge. It can create various temperature in the melt. By controlling the output power, the two-zone furnace can create a mushy zone area in the crucible, meanwhile, keep the temperature of the melt in the top part is higher than the liquidus temperature.
5.2. Statement of Problem

Set up and calibration of the two-zone furnace. Changing the output power of the two-zone furnace can create various temperature gradients. The furnace output power–temperature profile of different zones of the furnace is required for understanding the relationship between temperature gradients, cooling rates and microstructure formation.

A numerical model for the temperature profile in the system. Two-zone furnace system is useful to evaluate the UST influence on the mushy zone of the alloy during solidification process. However, it is hard to identify the mushy zone area in the furnace from the experiment precisely. A numerical model is developed to describe the temperature gradient in the crucible and help to predict the mushy zone.

The influence area of ultrasound. As indicated by Qian et al. [107], influence of ultrasound on melt decreases with increasing distance from the radiator. In this study, the height of the two-zone furnace crucible is larger than 300 mm, which is large enough to identify the influence of ultrasound. Adding ultrasonic treatment into two-zone furnace will be helpful to identify the ultrasound influence area. Based on the experimental results, the coefficient of ultrasonic attenuation (absorption) is studied quantitatively.

5.3. Experimental Approach

Aluminum alloy A356 was selected as the metallic alloy matrix. A schematic diagram of the two-zone furnace is shown in Figure 5.1.

Two-zone furnace system parameters are as follows: Maximum power for the top/bottom zone is 10 kW; height between bottom coil and base is 83 mm; height of top/bottom coil is 152 mm; gap between the top and the bottom zone is 32 mm, total height of the furnace is 425 mm. A graphic crucible opened at both ends was used in the two-zone furnace system; the height of the crucible is 355 mm, the outside diameter of the crucible is 100 mm, the interior diameter of the
crucible is 75 mm. A water-cooled stainless-steel chill block was applied at the bottom of the furnace as a cooling system of the crucible.

The ultrasonic equipment parameters are as follows: maximum power is 2.4 kW; frequency is 18 kHz, the diameter of the Nb ultrasonic probe is 40 mm and the probe amplitude is 20 microns. Three K-type thermocouples were fixed at different position of the crucible to record the temperature change, as shown in Figure 5.2. Thermocouple 1 is located at 50 mm from the bottom, thermocouple 2 is located at about 165 mm from the bottom, thermocouple 3 is located at about 270 mm from the bottom. Thermocouple wires were sealed in ceramic tubes to protect them from the molten alloy.

Figure 5.1. Schematic diagram of two-zone furnace system.
Two different types of experiments were carried out. (1) Non-treatment UST processing, (2) UST processing. Non-treatment UST processing group is the control group. In the control group, 3.3 kg A356 alloy was melted in the two-zone furnace. When alloy was totally melted, three coated thermocouples were inserted into the designed positions. Adjusted the top/bottom zone output power to create the temperature gradient in the furnace and recorded the temperature change. Top and bottom zone output power was adjusted to the maximum while temperature record finished when top melt reached about 750°C (thermocouple 3 is about 750°C), shut down the furnace to cool down the melt in the crucible to room temperature. In UST processing group, 3.3 kg A356 alloy was melted with maximum top/bottom output power. When alloy was totally melt, three coated thermocouples were inserted into the designed positions (same positions with non-treatment UST processing). During heating, ultrasonic probe was inserted into the melt about 30mm from the melt surface. When the top melt temperature reached about 750°C (thermocouple 3 is about 750°C), switched off furnace power and turned on ultrasound. UST was
applied into the melt until top melt temperature was 630°C. Treated melt cooled in the furnace to room temperature. The ultrasonic probe was inserted to about 20 mm below the melt surface.

The cast ingots are cylindrical in shape, height of casting cylinders is about 273 mm. Cylinders were cut into 17 disks, and labeled as C1-C17 (control group) and U1-U17 (UST group) from bottom to top, each piece height is 15-16 mm. The samples were mechanical ground using #300, #600, #800 and #1200 grinding papers, respectively. Then they were polished with 3 μm and 1 μm diamond polishing agents. The microstructure of the cast samples was characterized in detail via Optical Microscope (Nikon Model Epiphot 200).

5.4. Experimental Results

5.4.1 Output Power – Temperature Relationship

In the control group, furnace power and melt temperature relationship has been studied. The results are listed in Table 5.1. Table 5.1 indicates that due to the chill block on the bottom of crucible, there exists a temperature gradient when the top/bottom zone has a same output power. Changing top/bottom zone output power changes the temperature gradient in the crucible. The cooling curves of the control group and the UST group are shown in Figure 5.3. Figures 5.3 (a) and (b) show that the UST group has similar temperature changes with the control group. Top and middle section cooling curve in Figures 5.3 (a) and (b) are similar with the curve that shown in Figure 3.9, where the liquidus temperature is about 614°C. However, cooling curve of bottom section in Figures 5.3 are different with other curves. The reason is that the chill block that set on the crucible bottom affect melt bottom area and makes the melt of this area to have a larger cooling rate. UST was applied from top section, and stopped when the temperature of top melt reached about 630°C. According to Figure 5.3, when top melt temperature is about 630°C, temperature at thermocouple 2 is 621°C, and temperature at thermocouple 3 is 578°C.
Table 5.1 Experimental results about the output power and temperature relationship

<table>
<thead>
<tr>
<th>Top output power (kw)</th>
<th>Bottom output power (kw)</th>
<th>Thermocouple 1 (°C)</th>
<th>Thermocouple 2 (°C)</th>
<th>Thermocouple 3 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5</td>
<td>660</td>
<td>685</td>
<td>708</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>700</td>
<td>733</td>
<td>765</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>717</td>
<td>756</td>
<td>780</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>707</td>
<td>688</td>
<td>686</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>668</td>
<td>730</td>
<td>770</td>
</tr>
</tbody>
</table>

Figure 5.3. The cooling curves of (a) control group and (b) UST group.

ANSYS Fluent has been used to simulate the temperature profile in the two-zone furnace. The geometry of the model is the graphite crucible size. The model parameters are as follows: height of the model is 305 mm, diameter of the model is 75 mm, thermal conductivity is 90 $w m^{-1} K^{-1}$, viscosity is 0.03 $Kgm^{-1}s^{-1}$. Simulation time is 300 seconds, time step is 0.5 seconds.

The two-zone furnace consists of a top heating zone and a bottom heating zone. For top heating zone, the heat balance equation in steady state can be simplified to equation (7):

$$H = P * e + R$$  \hspace{1cm} (7)
where \( H \) is the heat generation (unit is W), \( P \) is the output power of each coil, \( e \) is the efficiency of the furnace, and \( R \) is the thermal radiation (unit is W). The induction furnace efficiency is about 0.35-0.40 [134]. According to the Stefan-Boltzmann equation, \( R \) is proportional to the fourth power of temperature. In this case, when temperature is about 700°C, \( R \) is about 3500 W-4500 W. For the bottom coil, the energy lose is the thermal radiation and the heat transfer with chill block. Assuming the temperature of chill block is constant (20°C). Accordingly, total energy lost is about 53000 W – 55000 W.

The simulation results are listed in Table 5.2. The simulation temperatures are very close to the experimental data (Table 5.1), except group top=5 kW and bottom=10 kW.

<table>
<thead>
<tr>
<th>Top output power (kW)</th>
<th>Bottom output power (kW)</th>
<th>Thermocouple 1 (°C)</th>
<th>Thermocouple 2 (°C)</th>
<th>Thermocouple 3 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5</td>
<td>654</td>
<td>695</td>
<td>711</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>696</td>
<td>738</td>
<td>757</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>717</td>
<td>759</td>
<td>779</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>712</td>
<td>736</td>
<td>720</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>659</td>
<td>719</td>
<td>771</td>
</tr>
</tbody>
</table>

Figure 5.4 is the simulation temperature distribution under different output power levels. It shows that the temperature has a similar distribution when the top power equals to the bottom power. Additionally, the simulated temperature profiles are shown in Figure 5.5. Three vertical dashed lines indicate the positions of the inserted thermal-couples in the experiment. X-axis of the curve is the distance from the crucible bottom.
Figures 5.4 and 5.5 illustrate that a mushy zone (temperature \(\leq 614^\circ\text{C}\)) can be created in the two-zone furnace. When top=5 kW and bottom=5 kW, the height of the mushy zone is about 20 mm.
Figure 5.4. Simulation temperature distribution under different output power.

Figure 5.5. Simulation temperature profiles under different output conditions (where T means top zone and B means bottom zone).
5.4.2 The Influence Zone of the Ultrasound

The microstructures of specimens taken from different locations of the casting ingot have been studied. Part of the results are shown in Figure 5.6.

The microstructure of C4 is dendritic grain morphology. Some dendritic grains were found in specimen C3, while globular grain also was found in C3. The microstructure difference between C4 and C3 is due to the cooling rate difference, which means the area of the chill block that strongly influence the casting microstructure is from C1 to C3.

Microstructure comparison results of both the control group and the UST processing group indicate that the UST influence area is from U16-U6. Microstructures of specimens U5-U1 are similar with that of specimens C5-C1. Microstructure of specimen U17 is a dendritic grain morphology with several large size gas holes. The microstructure difference between specimens C16-C6 and specimens U16-U6 shows that by applying UST during the solidification process can help to refine/modify the casting microstructure from dendritic grains to globular grains. The grain size of the UST processed specimen decreases significantly compared with that of the control group specimen at the same position.
Figure 5.6. The microstructure of specimens from different locations of the cast ingots (specimens labeled with C are from the Control group, specimens labeled with U are from the UST group).

5.5. Discussion

5.5.1 Refinement of Microstructure by Chill Block Cooling and UST Processing

The microstructure of specimens C1 consists of small globular grains. While specimens C2 and C3 have small dendritic grains and globular grains. The microstructure of other specimens in the control group is similar and consists of large dendritic grains. The difference between C3-C1 and other specimens is due to the cooling rate difference. The fast cooling rate refined the microstructure.

The microstructure of the specimen U17 consists of very large dendritic grains and gas holes. This can be explained as follows: specimen U17 is not affected by the ultrasonic cavitation because it is an area located above the ultrasonic radiator-melt interface, therefore U17 should have a similar microstructure with C17. Moreover, by removing the UST probe at the end of UST processing will introduce gas into the melt and can cause the gas holes shown in U17 microstructure.
5.5.2 Ultrasonic Attenuation in Molten A356 Alloy

Chapter 3 indicates that because of the attenuation (absorption) of the ultrasound in the melt, the ultrasonic intensity decreases with increasing distance from the radiating face. As mentioned in the literature review section, equations 4 and 5 can be used to calculate the ultrasonic attenuation in molten A356 alloy [114, 129].

\[
I = \frac{1}{2} \rho c (2\pi f A)^2
\]  
(4)

and

\[
I_x = I_0 e^{-2\alpha x}
\]  
(5)

where \( \rho \) is the liquid density, \( c \) is the sound velocity in the liquid, \( f \) is the ultrasonic frequency and \( A \) is the amplitude of ultrasound, \( I_0 \) is the initial ultrasonic intensity or the ultrasonic intensity at the ultrasonic radiator-melt interface, \( \alpha \) is the attenuation coefficient. In this case, \( \rho \) of molten A356 alloy is \( 2.67 \times 10^3 \text{ kg m}^{-3} \), \( c \) is \( 4.9 \times 10^3 \text{ m s}^{-1} \), \( f \) is 18 kHz and \( A \) is 20 \( \mu \text{m} \).

Assuming the radiating face is fully wetted by the melt, the maximum ultrasonic intensity at the ultrasonic radiator-melt interface \( I = 3344 \text{ W cm}^{-2} \). In general, ultrasound applied into light metals and alloys requires intensity \( I \geq 80 - 100 \text{ W cm}^{-2} \) above which fully developed cavitation occurs leading to significant structural refinement [99, 113, 114]. In this study, the influence area of ultrasound is from the radiator-melt interface to specimen U6 (from specimen U16 to U6). The influence area in this case indicates that when \( x \) is about 165 mm, \( I_x \leq 80 - 100 \text{ W cm}^{-2} \). The attenuation coefficient \( \alpha \) can be calculated: \( \alpha = 0.0113 \text{ mm}^{-1} (I_x = 80 \text{ W cm}^{-2}) \) or \( \alpha = 0.0106 \text{ mm}^{-1} (I_x = 100 \text{ W cm}^{-2}) \).
5.6 Conclusions

The ANSYS Fluent model was used to predict the temperature gradient of the A356 melt in the two-zone furnace under specific output power conditions. The simulation results fit very well the experimental data.

A mushy region can be created by the two-zone furnace. The height of the mushy zone is about 20 mm when the bottom coil power is 5 kW.

The ultrasonic attenuation coefficient has been determined based on the experimental data performed in this study.
CHAPTER 6 - CONCLUSIONS AND CONTRIBUTIONS OF THIS STUDY

6.1 Conclusions

This study has three sections. First, the influence of the process with the application of the UST during solidification on the microstructure of the matrix in A356-based nanocomposites has been studied. Second, the influence of the UST application on the morphology, size, and distribution of the Fe-rich intermetallics in aluminum A383 alloys has been identified. A two-zone furnace has been set up in the Ultrasonic and Solidification Processing Laboratory. Meanwhile, a numerical model has been developed to predict the temperature gradient in the graphite crucible.

These studies reveal the following:

1. The application of UST during alloy solidification process can decrease the grain size and change the primary phase morphology from dendritic grains to globular grains in the as-cast A356-based nanocomposites.

2. The UST application temperature/temperature range is an important factor that can significantly influence the grain refinement results in the nanocomposites. By applying UST at higher temperatures (higher than the liquidus temperature of the alloy) will enhance the nucleation rate. By applying UST at temperatures lower than the liquidus temperature of the alloy will cause dendrite fragmentation. The enhanced nucleation rate decreases the size of the dendritic grains in the casting but cannot change the grain morphology from dendritic to globular. Only if the dendrite fragmentation process occurs, globular grain morphology can be obtained in the as-cast alloys.
3. The optimum operation of the UST application in the A356-based nanocomposites should begin above the alloy liquidus temperature and end when the temperature decreases below the alloy liquidus temperature.

4. In the A383 alloys, the sludge phase will precipitate before the formation of the primary Al phase. The current experimental study indicates that by applying UST in the molten A383 alloy is an effective method to modify the sludge morphology as well as to decrease the sludge size and disperse the sludge uniformly into the melt.

5. The UST application temperature/temperature range during the solidification process has a strong effect on the morphology and distribution of the Fe-rich intermetallics in A383 alloy. The most effective UST application temperature for A383 alloy is 600 °C, which is after the sludge precipitation.

6. A two-zone furnace system can produce the required temperature gradient in the graphite crucible to successfully create a mushy region in the crucible.

7. A numerical model has been developed and validated using the experimentally measured data. The comparison between the simulations and experimental results indicates that the temperature profiles of the melt under specific heating power conditions can be accurately predicted. This model can be used in a future study to predict the temperature profiles in various locations in the crucible.

6.2 Main Contributions of this Study

1. A detail literature review has been performed, which revealed the UST effects on the metallic alloys.

2. The influence of UST application temperature/temperature range on the microstructure refinement of A356-based nanocomposites has been studied.
3. The precipitation temperature interval of the pre-dendritic Fe-rich intermetallics in A383 alloy has been identified.

4. The influence of the UST application temperature/temperature range on the sludge formation has been investigated.

5. A new two-zone furnace system has been set up.

6. A numerical model has been developed to determine the output power–temperature relationship in the two-zone furnace system.

7. The ultrasonic attenuation coefficient in A356 melts has been determined based on experimental data performed in this study.

6.3 Recommendations for Future Work

The effects of the UST application during the alloy solidification process on the alloy/nanocomposite primary phase microstructure have been studied in detail in this work. However, the effects of UST on the eutectic phase morphology (eutectic Si phase in Al-Si alloys) is not clearly understood. Future studies can focus on the eutectic Si phase evaluation under the UST application. In addition, the mechanical properties of the as-cast ingot including hardness, elongation, ultimate tensile strength, yield strength, fatigue life, wear resistance, etc., need to be evaluated.

The output power and temperature profiles of the two-zone furnace were evaluated in this study. It was shown that the cooling rate of each zone has no significant difference (except for a small area above the chill block), which leads to microstructure similarities in the cast ingot. To create a larger mushy zone, a precise control of the temperature gradients in the furnace are required. This can be designed by carefully adjusting the output power of each zone. Cooling
rate-microstructure relationship needs to be determined. Additionally, the ultrasound influence area and the ultrasonic attenuation coefficient in the mushy zone needs to be determined as well.
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