I. INTRODUCTION

**Grain** size is one of the most important factors that influences the processing and properties of Al alloys, and grain refinement is considered to be the foremost technique for achieving improvement in the quality of cast products, eliminating coarse and columnar grains, minimizing casting defects such as hot tear or macrosegregation, and facilitating downstream processing of the cast products. From the various grain refinement techniques, the most common practice is the addition of specialized master alloys containing potent nucleation substrates (AlTiB, AlTiC, AlB), primary intermetallics (Al1Ti, Al3Nb, etc.), and/or growth-restricting alloying elements (Ti, V, Nb, etc.). In current industrial practice, Al-Ti-B (Al-Ti-TiB) and Al-Ti-C (Al-Ti-TiC) master alloys are the most common grain refiners used in cast and wrought Al alloys. The grain refinement mechanisms as well as some technological issues related to Si or Zr poisoning of Al-Ti-B grain refiners are thoroughly scrutinized by theoretical models and experiments. Despite the commercial success of Al-Ti-B and Al-Ti-C grain refiners, some drawbacks are related to their application such as reduced performance in high-Si or Zr-containing alloys and agglomeration of borides in Al-Ti-B master alloys and a narrow process-parameter window for Al-Ti-C master alloys. A search for new grain refining systems that may substitute that currently used is ongoing. In recent times, interest has grown on using oxides such as Al2O3, MgAl2O4, and MgO as nucleation substrates in Al. It is well known that these oxides are formed naturally on the aluminum melt surface as stable layers, being thermodynamically stable and having sufficiently good crystallographic match with solid aluminum to act as substrates for its nucleation. Similarly, these oxides can be formed in situ as a reaction product of externally added oxide particles and liquid aluminum. In the case of thermodynamically unstable oxides (e.g., volatile oxides such as SiO2) added externally in liquid aluminum, formation of stable oxide crystals can be maximized by complete conversion of the volatile oxides. The same reactions were demonstrated upon conversion of volatile oxides into interconnected fibers of MgAl2O4 (spinel) phase in an Al alloy by self-propagating, high-temperature synthesis of powder compacts.

It was reported that oxide particles work better as nucleating substrates when the melt is subjected to an external physical field. Atamanenko et al. reported improved nucleation of aluminum on synthetic Al2O3 particles after ultrasonic cavitation melt processing. Li et al. demonstrated grain refinement of Al-Mg alloys using an intensive melt shearing technique and proposed a mechanism related to the dispersion of naturally occurring oxides such as MgAl2O4 in Al alloys. More recently, a significant reduction in grain size was observed in Al-MgAl2O4 in situ composite, presumably caused by MgAl2O4 crystals dispersed in aluminum by ultrasonic melt treatment.

This article reports on the manufacturing of an Al-MgAl2O4 concentrated master alloy and its application as a grain refiner in a commercially important cast alloy. First, the synthesis of the oxide-based grain...
refiner master alloy containing \textit{in situ} MgAl$_2$O$_4$ particles is described as based on the TiO$_2$ reaction with an Al-Mg melt assisted by ultrasonication. The reason for the selection of TiO$_2$ is twofold: (1) The new oxide-based master alloy (Al-Ti-MgAl$_2$O$_4$) contains free Ti as an important growth restriction element and MgAl$_2$O$_4$ as a nucleation substrate. (2) The grain refiner species are naturally formed by thermodynamically feasible reactions between Al-Mg melt and TiO$_2$ at practically acceptable processing temperatures. The possible mechanisms of the formation and dispersion of \textit{in situ} MgAl$_2$O$_4$ and Ti in Al are discussed and the grain refinement potential of the MgAl$_2$O$_4$ containing master alloy and its influence on the mechanical properties are examined for an A357-type casting aluminum alloy.

II. EXPERIMENTAL PROCEDURE

Commercially pure (CP) Al (0.08 wt pct Si, 0.1 wt pct Fe, remaining Al) and CP Mg (99.97 wt pct) were taken as initial metals. TiO$_2$ (Rutile) was chosen as a solid oxygen source for MgAl$_2$O$_4$ formation. TiO$_2$ is not stable in liquid aluminum and readily reacts with it to form Al-based oxides.\textsuperscript{[22]} The particle size of the TiO$_2$ supplied by Sigma-Aldrich varied from 0.5 to 10 \(\mu\text{m}\) (more than 80 pct between 1 and 5 \(\mu\text{m}\)). A total of 2 wt pct of TiO$_2$ particles was stirred in a molten Al-1.5 wt pct Mg alloy at temperatures between 923 K and 973 K (650 \(^\circ\text{C}\) and 700 \(^\circ\text{C}\)) using a mechanical impeller made from a Ti alloy and coated with a high-temperature ceramic material to minimize impeller erosion during processing. The total volume of the processed melt was 1 kg. After stirring and mixing, the melt was heated and held at 1173 K (900 \(^\circ\text{C}\)) for 30 minutes to facilitate the reaction between oxide particles and liquid Al–Mg alloy. Then temperature was decreased to 973 K to 993 K (700 \(^\circ\text{C}\) to 720 \(^\circ\text{C}\)), and the melt was subjected to ultrasonic processing (water-cooled Reltec transducer, 17.5-kHz, 3.5-kW, 40-\(\mu\text{m}\) peak-to-peak amplitude, Nb sonotrode) while stirring with the impeller for 5 minutes to ensure the dispersion of formed MgAl$_2$O$_4$ particles and to complete the reaction of TiO$_2$ particles. The cycles of higher temperature holding and lower temperature mixing were repeated five times, and the final mixture was cast at 1023 K (750 \(^\circ\text{C}\)) in a steel round mold preheated at 473 K (200 \(^\circ\text{C}\)). The obtained cast sample would be used as a master alloy (MA), and its average chemical composition was estimated as follows. To measure the chemical composition, 10 g of the master alloy was diluted in 100 g of CP Al and cast in a metallic mold. The average Ti and Mg composition of the cast sample was determined from five measurements on the sample surface by optical emission spectrometry in Foundry Master. The MgAl$_2$O$_4$ content in the master alloy was calculated using the following reaction:

\[
[Mg] + 2[Al] + 2 <\text{TiO}_2 > = <\text{MgAl}_2\text{O}_4 > + 2[\text{Ti}]
\]  

The accuracy of chemical analysis was within 10 rel pct of the average measured value.

Grain refinement efficiency was assessed using an A357-type alloy (7.4 wt pct Si, 0.5 wt pct Mg, 0.1 wt pct Fe, 0.1 wt pct Ti, remaining Al) (500-g level). Different amounts of the master alloy (specified later in the text) were added to 500 g of the molten A357 alloy at 1033 K (760 \(^\circ\text{C}\)), and the melt was allowed to rest for 5 minutes. After that, the alloy was cast at 1023 K (750 \(^\circ\text{C}\)) in a steel mold (200 g, cooling rate ~2 to 3 K/s (2 to 3 °C/s)) preheated to 523 K (250 \(^\circ\text{C}\)). The dimensions of the mold as well as the section where the metallographic samples were taken are shown in Figure I. In addition to the described experiments, the A357 alloy with and without additions was treated with ultrasound for 3 minutes at 1013 K to 1023 K (740 \(^\circ\text{C}\) to 750 \(^\circ\text{C}\)) prior to casting (ultrasonic processing parameters were the same as shown earlier for the master alloy). For comparison, the grain refinement of the A357 alloy was studied after additions of an Al-5 pct Ti-1 pct B master alloy (London Scandinavian Metallurgical Co. Ltd) with all other conditions retained. At least two castings were produced for each condition. The cast samples were ground using SiC paper (400 to 2500 grid size) and polished using OPS. For identification of grain size, polished samples were anodized using 4 pct HBF$_4$ solution for ~1 minutes at 20 VDC and analyzed in polarized light in an optical microscope (Zeiss Axioscope). The microstructure of the master alloy was investigated using optical microscopy (OM) (Zeiss Axioscope) and scanning electron microscopy (SEM) (Zeiss Supra 35VP), and phase identification was performed using X-ray diffraction (XRD) (Bruker D8 Advance) and energy-dispersive spectroscopy (EDS) (EDAX).

Grain size was determined using the conventional linear intercept method with 50 to 100 grains measured in each sample and with the statistical analysis of the data performed (error bars are shown in relevant plots). The size of the particles was also measured using the linear intercept method with 20 to 50 particles measured and with the statistical error not exceeding 10 rel pct of the average.

Thermal analysis during solidification of selected samples with and without addition of the master alloy was performed using K-type 0.5-mm thick thermocouples and NI-LABVIEW Data Logger capable of collecting 100 data points per second. The accuracy of the temperature measurement was within 0.5 K (0.5 °C). The same steel mold used for grain refinement study was covered with ceramic wool to minimize the temperature loss and preheated to 623 K (350 °C). The thermocouple was positioned from the top between the center and the wall of the mold. The metal was poured at a superheat of 100 K (100 °C) above the liquidus of the alloy. Each experiment was repeated three times with good reproducibility of the results.

Tensile tests of machined specimens (four samples for each condition) were carried out in Instron 5569 with a 50-kN load cell (ASTM E8). The sample dimensions were according to ASTM standard B557-06. Rectangular specimens with gauge length 25 mm were machined from the billet cast in a permanent steel mold (1-kg melt charge). The casting conditions (temperature, melt
Prior to testing, all test bars were heat treated. The samples were annealed for 12 hours at 813 K (540 °C), water quenched [warm at 323 K (50 °C)], and subsequently aged at 443 K (170 °C) for 12 hours. Elongation of the samples was recorded using an external extensometer (25-mm gauge length), and yield stress was calculated by the 0.2 pct offset method. At least four samples were tested for each condition, and statistical analysis of the data was performed.

### III. RESULTS AND DISCUSSION

#### A. Synthesis of an Al-Ti-MgAl₂O₄ Master Alloy

1. **Chemical and phase composition of the synthesized master alloy**

The average chemical composition of the master alloy was estimated from the chemical analysis as Al-0.6 wt pct Mg-1.3 wt pct Ti-1.8 wt pct MgAl₂O₄. We can see that 1.3 wt pct of free elemental titanium was released after the reaction between 2 wt pct TiO₂ and Al according to Eq. [1]. The range of Ti detected in various samples was between 1.2 and 1.5 wt pct probably as a result of a minor Ti dissolution from the impeller. Also, 0.6 wt pct Mg was found to remain in the alloy after the reaction and oxidation (burning) at higher temperatures. Figure 2 shows the microstructures of the Al-Ti-MgAl₂O₄ master alloy prepared by the *in situ* synthesis. MgAl₂O₄ particles (dark spots) were found dispersed mostly as small clusters in the Al matrix (Figures 2(a) and (b)). Clusters of 10 to 20 μm were also identified everywhere in the cast billet, although large ones (>50 μm) were rarely observed. Al₃Ti blocks and platelets (pointed by arrows) were found distributed in the matrix alloy (Figures 2(a) and (b)). Al₃Ti particles were also identified within the clusters of MgAl₂O₄ as illustrated in Figure 2(c). In general, the microstructure of the master alloy is comparable with that of a commercial Al-5Ti-1B master alloy where Al₃Ti blocky particles of size ~50 μm and fine TiB₂ particles were distributed throughout the matrix (Figure 2(d)). The presence of MgAl₂O₄ and Al₃Ti phases is confirmed in Figures 3, 4, and 5. An XRD pattern of the cast billet showed only MgAl₂O₄ and Al₃Ti peaks in the master alloy (Figure 3). No unreacted TiO₂ particles were

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Fig. 1—Schematic of metallic mold used for grain refinement studies.

Fig. 2—Optical micrographs of (a through c) Al-Ti-MgAl₂O₄ master alloy and (d) Al-5Ti-1B master alloy.
The formation of MgAl$_2$O$_4$ and Al$_3$Ti in the master alloy was confirmed also by SEM coupled EDS analysis (Figures 4 and 5). The size of MgAl$_2$O$_4$ particles varied from a few hundred nm to 1 to 2 μm. Similarly, most Al$_3$Ti particles were found to be between 1 and 20 μm in size.

2. Formation of MgAl$_2$O$_4$ in the master alloy

The Al$_2$O$_3$-MgAl$_2$O$_4$-MgO phase equilibria was studied by thermodynamic models and experimentally verified with different Mg compositions of matrix alloy elsewhere.

The studies established that Al$_2$O$_3$ forms at very low Mg content (<0.19 wt pct), whereas MgAl$_2$O$_4$ is stable between 0.007 and 10 wt pct Mg and MgO is stable at >7 wt pct Mg. Hence, in the Al-1.5 wt pct Mg-2 wt pct TiO$_2$ composition used in the present study, only MgAl$_2$O$_4$ can be stable, which was confirmed by XRD analysis (see Figure 3). The synthesis of spinel is initiated by reactive wetting through Eq. [1] as it results in the reduction in interfacial energy ($\Delta G^\circ = -273$ KJ/mol at 1123 K (850 °C)) by the formation of MgAl$_2$O$_4$ at the liquid Al-TiO$_2$ interface (event (a) in Figure 6).

After the formation of the first layer of MgAl$_2$O$_4$, Mg, Al, and Ti must diffuse through the layer to enable a further reaction at the interface of the TiO$_2$ particle. The reactive wetting continues until the particle surface is completely reacted. When MgAl$_2$O$_4$ crystals get accumulated and cover the entire TiO$_2$ particle surface, the reaction is likely to cease. Small MgAl$_2$O$_4$ crystals of a few hundred nm bonded by Van der Waals force remain clustered on the surface of a TiO$_2$ particle (event (b) in Figure 6). This mechanism is very similar to the formation and clustering of MgAl$_2$O$_4$ crystals on SiO$_2$ particles reported elsewhere.

In a parallel process, Ti atoms are released from TiO$_2$ and diffuse into molten Al. Fine Al$_3$Ti blocks (1 to 2 μm) clustered along with MgAl$_2$O$_4$ particles in partially dispersed agglomerates (Figures 2(c) and 5) testify for Al$_3$Ti formation during the reaction. The migration of Ti atoms across the TiO$_2$-Al interface initiates the overall diffusion process in the Al–Ti alloy system but also can produce a saturated solution adjacent to the interface as a result of low solubility of Ti in Al (~0.8 wt pct at 1173 K (850 °C)], resulting in the nucleation of the Al$_3$Ti phase at the interface. Fine Al$_3$Ti particles grow to larger ones either by interdiffusion of Al and Ti or by coalescence of fine Al$_3$Ti particles as shown by arrows in Figure 5. Thus, the complete reaction of TiO$_2$ with the Al-Mg melt is not possible without efficient dispersion of MgAl$_2$O$_4$ and Al$_3$Ti, enabling the progression of the reaction, and ultrasonic cavitation was found to facilitate the process.

3. Effect of ultrasonication on dispersion of particles

Ultrasonic processing was used as part of the procedure to synthesize the master alloy. The analysis of the master alloy showed that the TiO$_2$ particles reacted completely and that MgAl$_2$O$_4$ particles and fine aggregates were dispersed within the matrix. The influence of...
ultrasonic cavitation and acoustic streaming on the dispersion of ultrafine particles in molten metal has been studied elsewhere.\textsuperscript{[25,27–30]} It was experimentally demonstrated that the cavitation threshold pressure reduced from 800 to 550 kPa with the increase in alumina concentration in an aluminum melt from 0.005 to 0.1 wt pct.\textsuperscript{[27]} In the present experimental conditions, particles of TiO\textsubscript{2} and reaction products and gases absorbed on their surface act as nucleation sites for cavitation. Recently, Tzanakis \textit{et al}.\textsuperscript{[31]} reported that acoustic pressures exerted from the activity of the cavitation bubbles in liquid aluminum could be as high as 800 kPa, which may be sufficient to break the cluster of particles facilitating the de-agglomeration process and wetting. Cavitation and acoustic flows generated by the cavitation regions in a particle-populated molten metal may trigger the following events in the process under current investigation: (1) disintegration and distribution of loose TiO\textsubscript{2} agglomerates, (2) improved wetting and accelerated displacement reaction at particle interfaces, and (3) removal of MgAl\textsubscript{2}O\textsubscript{4} clusters and the Al\textsubscript{3}Ti phase from the reacted zone exposing a new diffusion zone for further reaction (event (c) in Figure 6). The mechanism is similar to the ultrasonic dispersion of \textit{in situ} MgAl\textsubscript{2}O\textsubscript{4}\textsuperscript{[21]} and \textit{in situ} Al\textsubscript{3}BC\textsuperscript{[32]} crystals in Al-Mg-SiO\textsubscript{2} and Al-B-graphite alloys, respectively.

Particles of Al\textsubscript{3}Ti are apparently refined during ultrasonic processing at 973 K to 993 K (700 °C to 720 °C). To confirm the cavitation-induced fragmentation of Al\textsubscript{3}Ti, 100 g of master alloy was remelted at 1173 K (900 °C) and cast without ultrasonication. Large Al\textsubscript{3}Ti needles over 200 \textmu m in size were formed in the master alloy (Figure 7).

B. Grain Refinement of an A357 Alloy

1. Effect of master alloy additions and ultrasonic melt processing on the grain size

Figure 8 shows the microstructures of an anodized A357 alloy without additions. The average grain size of the unrefined alloy was 900 \textmu m (Figure 8(a)). With the application of ultrasound but without master alloy
additions, the grain size of the alloy was found to be similar (Figure 8(b)). Upon the addition of 0.25 wt pct master alloy, the grain size was reduced to 640 μm (Figure 9(a)). With further addition of master alloy from ~1.7 to 5.8 wt pct, grain size was reduced from 400 to 320 μm (Figures 9(b) and (c)). Application of ultrasonic processing gives further reduction of the grain size (~200 μm) at the higher addition levels of the master alloy; yet, the influence was less significant at the lowest addition (0.25 wt pct) (Figures 10(a) through (c)). The average grain size vs the amount of master alloy addition is shown in Figure 11. The plateau that represents the bottom limit of the grain size obtained with ultrasonication is about 200 μm and does not depend on the addition level from 1.7 wt pct onward. Figure 9 shows large pores and agglomerates in the microstructure of the grain refined alloys; nevertheless, defects are reduced appreciably after ultrasonic processing (Figure 10). This may be related to better distribution of spinel particles as a result of ultrasonic cavitation and induced flows as well as to the melt degassing by ultrasonic processing.[27]

To look at the significance of the new master alloy in grain refinement of A357 alloy, similar experiments were conducted with the addition of an Al-5Ti-1B master alloy. As the compositions of the two master alloys were different, the experiment with Al-5Ti-1B was conducted based on the similar free Ti content in the added master alloys. Free Ti content in the Al-Ti-MgAl2O4 and Al-5Ti-1B master alloys is ~1.3 and ~3 wt pct, respectively. The used additions of the master alloys and the corresponding free Ti concentrations are summarized in Table I.

The grain sizes of the A357 alloys with additions of either the commercial Al-5Ti-1B grain refiner or the spinel-based master alloy are compared on the basis of the free Ti in Figure 12. It is evident that at low addition levels, Al-5Ti-1B is more effective in grain size reduction than is the new oxide-containing master alloy. Nevertheless, at higher addition levels (equivalent to 0.02 wt pct of free Ti and beyond), both master alloys performed similarly. It is important to note that the amount of an Al-5Ti-1B master alloy required for achieving grain refinement is much lower than that of the oxide-containing master alloy in all the experiments (see Table I). Ultrasonication showed extra reduction in grain size at all additions. These observations are further confirmed from the microstructures of A357 alloys with different additions of the Al-5Ti-1B master alloy (Figures 13 and 14).

2. Mechanisms of grain refinement

Thermal analysis is usually used to assess solidification of alloys, as are those inoculated with potential grain refiner inoculants. Figure 15 presents the representative cooling curves of an A357 alloy with and without 2 wt pct addition of the Al-Ti-MgAl2O4 master alloy, cast in the same metallic mold to measure the undercooling and the nucleation temperature of the primary Al crystals. From these cooling curves, the nucleation temperature (Tn) of primary Al crystals is identified from the first derivative of the temperature (dT/dt) curve, where the slope of the T–t curve starts to deviate.[10] The other two characteristic temperatures are (1) Tmin, unsteady state growth temperature or the onset of recalescence, when the latent heat of solidification surpasses the heat extracted from the sample by cooling; and (2) Tg, the end of recalescence or the onset of steady state growth of primary (Al) dendrites. Consequently,
Fig. 9—Anodized micrographs of A357 cast without ultrasonication after inoculation of Al-Ti-MgAl₂O₄ (a) 0.25 wt pct, (b) 1.7 wt pct, and (c) 5.8 wt pct.

Fig. 10—Anodized micrographs of A357 cast with ultrasonication after inoculation of Al-Ti-MgAl₂O₄ (a) 0.25 wt pct, (b) 1.7 wt pct, and (c) 5.8 wt pct.
the undercooling of the primary (Al) nucleation can be approximated as $\Delta T = (T_g - T_{\text{min}})$. In the alloy without master alloys addition (Figure 15(a)), the (Al) primary phase starts to nucleate at 893 K (620 °C) and ends at 891.5 K (618.5 °C). The maximum nucleation undercooling from the recalescence was calculated to be 1.5 K (1.5 °C). In the presence of the Al-Ti-MgAl$_2$O$_4$ master alloy (Figure 15(b)), (Al) in the A357 alloy starts nucleating at a higher temperature of $\approx$896 K (623 °C) (up nearly by 3 K (3 °C)) and no nucleation undercooling was noticed in the cooling curve. It was reported earlier that the Ti presence in an inoculated A356 alloy increased its liquidus temperature and, hence, the nucleation started higher in the cooling curve. The absence of recalescence is not uncommon in Al-Si alloys inoculated with a higher amount of Al-5Ti-1B master alloy and at moderate cooling rates, e.g., 2 K/s (2 °C/s). This happens as a result of an increased number of heterogeneous nucleation events aided by numerous nucleant particles present in the alloy at higher additions of master alloy (2 wt pct here). Note that the limitations of the data acquisition and thermocouple sensitivity can sometimes neglect a small change in the temperature. The results of this thermal analysis testify that MgAl$_2$O$_4$ particles act as potent heterogeneous nucleation sites for aluminum.

The nucleation potency of a substrate is related to its lattice matching with solid Al during nucleation process. A closer lattice match refers to better nucleation potency. Lattice matching of MgAl$_2$O$_4$ with Al was experimentally reported to be a cube on a cube parallel orientation relationship (OR), or a mismatch of 2.5 deg along the [110] direction on the (111) plane between Al and MgAl$_2$O$_4$ with a theoretically calculated misfit of 1.4 pct. This mismatch was found to be smaller than that of the Al/TiB$_2$ system (~4.2 pct). The nucleation efficiency has also direct correlation with the number density and size distribution of particles and the undercooling (cooling conditions). According to the athermal heterogeneous nucleation theory, the nucleation undercooling, $\Delta T_g$, can be estimated by the equation:

$$\Delta T_g = 4\Gamma_d / D$$

where $\Gamma_d$ is the Gibbs–Thomson coefficient between the stable embryo of the solid phase and the liquid and $D$ is the diameter of the particle. For an Al alloy, $\Gamma_d$ is about $9.12 \times 10^{-8}$ K m. From Eq. [2], the undercooling required for MgAl$_2$O$_4$ crystals to nucleate aluminum can be calculated as 1.82 K (1.82 °C) for 200-nm particles and 0.18 K (0.18 °C) for 2-μm particles. It was also shown that for four contributions to the total solidification undercooling (kinetic, curvature, thermal, and solutal), the solutal or constitutional undercooling ($\Delta T_{cs}$) is the controlling term under typical aluminum alloy casting conditions. Maximum $\Delta T_{cs}$ for CP Al at a typical solidification velocity was calculated to be 2.8 K (2.8 °C) and assumed to be higher for more solute-containing alloys. The measured thermal undercooling is very small in the case of spinel-inoculated alloys (Figure 15). This means that the solutal component of undercooling plays the most essential role in nucleation on the MgAl$_2$O$_4$ substrates.

It is well known that with a spread of particle sizes, grain initiation events are also spread over a range of undercooling. A few early nucleation events triggered by larger particles can then lead to grain growth and latent heat evolution, rendering many smaller particles inactive. In was shown that in the Al-5Ti-1B master alloy, active TiB$_2$ particles constitute around 40 vol pct of the particles population but the number

![Fig. 11—Relation between grain size of A357 and the level of Al-Ti-MgAl$_2$O$_4$ master alloy addition.](image)

![Fig. 12—Relation between grain size of A357 and the free Ti from the added master alloys.](image)

| Table I. Master Alloy Additions and Corresponding Free Ti in Each Master Alloy, Respectively (in Wt Pct) |
|---------------------------------|-----------------|-----------------|
| Master Alloy Addition (Wt Pct) | Free Ti (Wt Pct) | Free Ti (Wt Pct) |
|---------------------------------|-----------------|-----------------|
| Al-Ti-MgAl$_2$O$_4$ 0.25, 1.0, 1.7, 4.2, 5.8 | 0.003, 0.012, 0.02, 0.03 | 0.00, 0.01, 0.02 |
| Al-5Ti-1B 0.1, 0.4, 0.7, 1.7, 2.4 | 0.05, 0.07 | 0.05, 0.07 |
efficiency of optimum sized particles is less than 1 pct. Furthermore, particles less than 500 nm in size do not take part in nucleation even under cooling rates as high as ~3.5 K/s (3.5 °C/s). At lower cooling rates, as in the study, ~2 to 3 K/s (2 to 3 °C/s), the minimum particle size will be much larger. Hence, the best nucleation...
efficiency under real casting conditions is achieved by decreasing the spread of particle distribution and increasing the particle size ideally to 2 to 5 μm. Our results show that MgAl<sub>2</sub>O<sub>4</sub> particles in the Al-Ti-MgAl<sub>2</sub>O<sub>4</sub> master alloy have a large spread of particle sizes, from a few hundred nm to 2 microns. For a particular free Ti level, the number density of MgAl<sub>2</sub>O<sub>4</sub> particles in the Al-Ti-MgAl<sub>2</sub>O<sub>4</sub> master alloy is higher than that of TiB<sub>2</sub> in Al-5Ti-1B. Nevertheless, the spinel-containing master alloy may largely contain very small particles (i.e., inactive particles), which negatively affects the nucleation efficiency of this master alloy. This is evident at lower additions of the master alloy where grain size was found to be larger than those produced with an optimized commercial Al-5Ti-1B grain refiner. More addition seemingly increased the number density required for the grain refinement to the level similar to Al-5Ti-1B. Yet, a large number of inactive particles in the Al-Ti-MgAl<sub>2</sub>O<sub>4</sub> master alloy did not contribute to
Table II. Mechanical Properties of A357 Alloy Inoculated with Different Master Alloys and Treated With Ultrasonication

| No | Alloy            | Yield Stress (MPa) | Ultimate Tensile Stress (MPa) | Elongation (Pct) |
|----|------------------|--------------------|------------------------------|------------------|
| 1  | A357             | 260 ± 8            | 314 ± 8                      | 5 ± 1            |
| 2  | A357-US          | 273 ± 5            | 326 ± 6                      | 6 ± 1            |
| 3  | A357-MA          | 278 ± 3            | 337 ± 9                      | 5 ± 2            |
| 4  | A357-MA-US       | 288 ± 4            | 349 ± 9                      | 8 ± 2            |
| 5  | A357-Al5Ti1B     | 272 ± 5            | 335 ± 10                     | 5 ± 2            |
| 6  | A357-Al5Ti1B-US  | 278 ± 7            | 340 ± 9                      | 7 ± 2            |

C. Mechanical Properties of A357 Alloys

Mechanical behavior of A357 alloys cast under different conditions, with and without grain refiner, is shown in Figure 18 and Table II.

A systematic improvement in both strength and ductility with respect to the addition of the oxide-containing master alloy and ultrasonication is obvious. A minimum of 10 and 50 pct increase in strength and ductility, respectively, was achieved in an A357 alloy inoculated with oxides and treated with ultrasonic cavitation in comparison with the reference alloy. Moreover, the strength and ductility of the oxide inoculated alloys are comparable with the alloys inoculated with an equivalent amount of Al-5Ti-1B master alloy (0.02 wt pct free Ti). In addition to the grain refinement of the inoculated alloys, the ultrasonic cavitation and streaming additionally contribute to the improvement of mechanical properties by reducing hydrogen porosity but redistribution of nonmetallic inclusions.

IV. CONCLUSIONS

1. An Al-1.3 wt pct Ti-1.8 wt pct MgAl2O4 master alloy was successfully manufactured using an ultrasonication-aided in situ synthesis. Complete reaction of the parent TiO2 oxide with a homogeneous bulk distribution of formed MgAl2O4 particles and their clusters was achieved by this methodology. Fine particles of Al2Ti (2 to 20 μm) were also formed and distributed in the alloy.

2. The master alloy is capable of grain refining an A357 alloy (Al-7 pct Si-0.5 pct Mg) by 25 pct. Ultrasonication is responsible for further grain refinement by 25 pct. Spinel particles in the master alloy provide substrates for aluminum nucleation, whereas free Ti restricts grain growth.

3. The master alloy showed similar grain refinement performance in comparison with a commercial Al-5Ti-1B master alloy if compared on the free added Ti level, albeit at a higher master alloy addition.

4. Grain refinement with oxide inoculation and ultrasonic processing of an A357 alloy resulted in at least 10 pct strength and 50 pct elongation improvement in comparison with the reference alloy and a similar mechanical performance in comparison with the alloys inoculated with Al-5Ti-1B master alloy.

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