

Identifying the stages during ultrasonic processing that reduce the grain size of aluminium with added Al₃Ti₁B master alloy**

By Gui Wang*, Matthew S. Dargusch, Dmitry G. Eskin, and David H. StJohn

[*] *Dr. G. Wang Corresponding-Author, Prof. M.S. Dargusch, Prof. D.H. StJohn
Centre of Advanced Materials Processing and Manufacturing (AMPAM), The University of
Queensland, St Lucia QLD 4072 Australia
E-mail: gui.wang@uq.edu.au*

*Dr. G. Wang, Prof. M.S. Dargusch, Prof. D.H. StJohn
Defence Materials Technology Centre (DMTC), Australia
Prof. D.G. Eskin*

BCAST, Brunel University London, Uxbridge UB8 3PH, United Kingdom

*Prof. D.G. Eskin
Tomsk State University, 634050 Tomsk, Russian Federation*

[**] *Mr. Sachin Malhotra and Mr. Paren Patel are acknowledged for their help during sample preparation. Financial support was provided by the Defence Materials Technology Center (DMTC) that was established and supported by the Australian Government's Defence Future Capability Technology Centres Programme, and ARC project DP140100702. Prof. Eskin thanks the ExoMet Project co-funded by the European Commission's 7th Framework Programme (contract FP7-NMP3-LA-2012-280421), by the European Space Agency and by the individual partner organisations. We also thank AMG Aluminium for the provision of Al₃Ti₁B master alloy.*

Abstract

The combined application of UST and Al₃Ti₁B grain refiner changes the macrostructure of untreated commercial purity aluminium from large millimetre sized columnar grains to equiaxed grains of a few hundred microns. This research revealed three distinct stages that affect the grain size while UST is applied during melting and solidification. Stage I applied well above the liquidus temperature improves the efficiency of the refiner, possibly by de-agglomeration and wetting of TiB₂ particles, and their distribution throughout the melt by acoustic streaming. Stage I is followed by Stage II where little further improvement occurs. Stage III causes additional grain refinement when applied at and below the liquidus temperature where nucleation of grains maybe enhanced by cavitation, which could also facilitate fragmentation and detachment of grains formed on the sonotrode. Convection due

to acoustic streaming creates a uniformly undercooled temperature in the melt, which ensures the survival of these new grains during transport, as well as assisting the transport of grains to produce a uniform fine grain size throughout the ingot.

Introduction

Continuing efforts to produce even finer grains in alloy microstructures are driven by the need to improve the thermo-mechanical performance of most metals, which in turn allows less metal to be used in manufacturing components, as well as reducing heat treatment and homogenisation times to improve productivity and energy efficiency of manufacturing processes. For commercial purity aluminium (CP Al) this goal is currently achieved by the addition of Al-Ti-B master alloys.^[1] The aim of this work is to understand the synergetic effect of ultrasonic treatment (UST) and addition of an Al₃Ti₁B grain refining master alloy as a possible method of achieving much finer grain sizes by improving the grain refining efficiency of the master alloy. Despite the practical issues in applying UST to large-scale industrial processes, interest in ultrasonic melt processing has been growing in recent years due to its environmental attributes of zero-emissions and energy-efficiency.^[2] The results of this study show that UST significantly refines the grain size when applied during two critical stages: well above the liquidus temperature and then as the melt cools below the liquidus temperature.

Upon addition of an Al-Ti-B master alloy numerous potent TiB₂ particles are released and dispersed into a melt with less than 1% of these particles nucleating Al grains.^[3, 4] The master alloy also releases solute Ti into the melt.^[5] Both forms of Ti are necessary to achieve a fine grain size.^[6] Given the low efficiency of master alloys, the application of UST has the potential to provide a greater level of additional refinement.^[7-11] When ultrasonic waves of sufficient amplitude and frequency move through the melt, the resulting acoustic cavitation is

believed to activate sites for heterogeneous nucleation and induce fragmentation and de-agglomeration, while acoustic streaming provides convection currents that distribute the nucleants and newly formed grains throughout the melt.^[11] These mechanisms acting together should further significantly reduce the grain size. In a previous study^[12] we examined the effect of a range of Al₃Ti₁B master alloy contents with and without ultrasonic treatment on grain size. The actual times and/or temperatures at which refinement was facilitated during cooling was not revealed by these experiments.

The principal response to UST of melts containing added grain refiner is attributed to the wetting of nucleant particles and de-agglomeration of the TiB₂ particle clusters above the liquidus temperature creating many more active nucleation sites.^[11] Other studies have shown that UST induces significant refinement when applied during cooling from just above to below the liquidus temperature.^[13, 14] This study will determine precisely when, during UST, nucleation is promoted and the relative contribution these mechanisms make to the final as-cast grain size.

Experimental

320-350 grams of CP Al ingot (99.7%) were melted in a graphite-clay crucible with 60 mm top diameter, 35 mm bottom diameter and 85 mm height by an electric resistance furnace. Additions of an Al₃Ti₁B master alloy at concentrations of 50 or 200 ppm Ti were introduced into the molten melt at 740±3°C, which was then stirred and held for 5 minutes before being transferred to the UST platform (details reported in ^[14]). When UST was not applied the alloy was allowed to cool and solidify in the crucible without the insertion of the sonotrode.

For the UST experiments, the ultrasonic device consisted of a 1.5 kW commercial ultrasound generator, an air cooled 20-kHz piezoelectric transducer and a sonotrode made of a molybdenum alloy with an 18-mm diameter tip. The ultrasonic device produces frequencies

and amplitudes well above the threshold for cavitation, which occurs in a region just below the sonotrode^[11]. When UST was applied, the sonotrode was switched-on without preheating and then immersed 10 mm below the top surface of the melt in the graphite-clay crucible. Based on previous research,^[14] the sonotrode was heated by the melt to near the melt temperature in about 20 s. One K-type thermocouple was inserted into the melt beside the sonotrode. The UST experiments were conducted with a fixed power input of 0.75 kW at a peak-to-peak amplitude of 20 μm applied during cooling from 720 °C, which is 60°C above the liquidus temperature of CP aluminium, and UST was stopped at various temperatures above and below the liquidus temperature. The effect of time over which UST was applied was also measured.

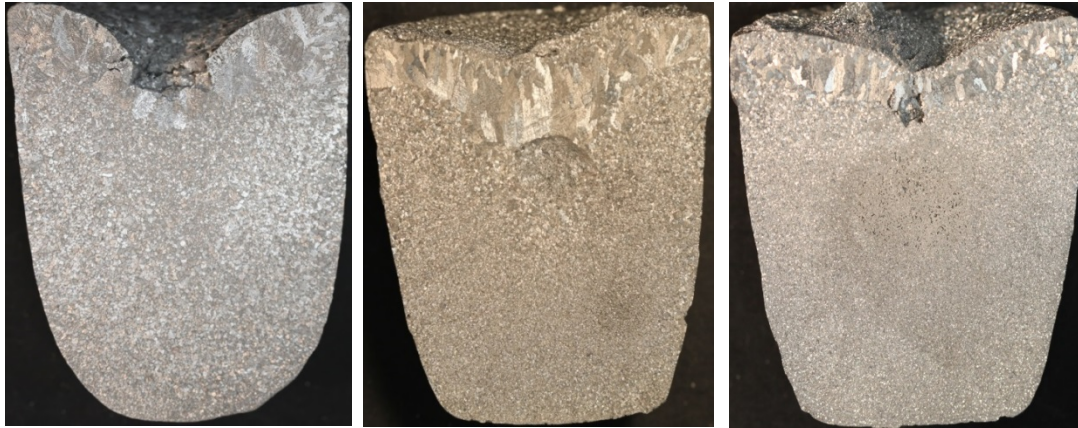
A data-acquisition system with a sampling rate of four readings per second collected the temperature data. The cooling rate above the liquidus temperature was 0.45-0.55 °C/sec without UST and 0.72-0.96 °C/s with UST. The faster cooling rate would make a difference to the amount of refinement that occurs during the nucleation phase when ultrasonic treatment is not applied. Based on other work^[15] this change in cooling rate would reduce the grain size by about 10%. In comparison, when UST was applied in this study, the grain size was observed to decrease by about 50%. Macrographic samples sectioned along the centre symmetrical axis of the solidified casting were mechanically ground and polished for observation. The grain size was measured using the linear intercept method (ASTM E112-10) on small metallographic samples cut at 45 mm from the bottom of the sectioned piece (i.e. the same height as the thermocouple tip position and 25 mm below the sonotrode). Micrographs were obtained by a Leica Polyvar microscope with polarized light after anodizing using a 0.5% HBF_4 solution for about 20 seconds at 30 V. The grain size was converted to grain density (number of grains per cm^3) which is a measure of the number of successful nucleation events in a volume of melt. The conversion is $GD=0.74 \times GS^{-3}$ where GD is grain density, and GS is

grain size).^[16] It should be noted that this number density is not related to the number density of TiB_2 particles (typically less than 5 microns) released by the $\text{Al}_3\text{Ti}_1\text{B}$ master alloy, which is two orders of magnitude larger than the grain density.

Results

Without the application of UST, CP Al typically solidifies as large columnar grains of the order of millimetres in size.^[17] Solidification of CP Al with the addition of the master alloy at 50 ppm Ti produced a coarse equiaxed macrostructure as shown in Figure 1a. Figure 2a shows the typical equiaxed grain structure obtained from the centre of the ingot with a measured average grain size of $278 \pm 20 \mu\text{m}$.

Upon application of UST to the grain refined samples from 720 to 700°C which is 60 to 40°C above the liquidus temperature of CP Al, the macrostructure (Figure 1(b)) presents a uniform fine grained structure throughout the whole ingot. The average grain size in the centre of the ingot is about $214 \pm 12 \mu\text{m}$ (Figure 2(b)), indicating that a 23% improvement in grain refinement results from the application of UST well above the liquidus temperature. On extending the UST temperature range to 720 to 660°C (the liquidus temperature), the macrostructure can be further refined (Figure 1(c)) to an average grain size of $130 \pm 8 \mu\text{m}$ (Figure 2c). An increase in the amount of $\text{Al}_3\text{Ti}_1\text{B}$ to 200 ppm Ti, reduced the grain size to $150 \pm 11 \mu\text{m}$ without UST and to about $116 \pm 10 \mu\text{m}$ with UST. Thus, increasing both the UST temperature range to include the liquidus temperature and the amount of master alloy addition result in significant reduction in grain size.

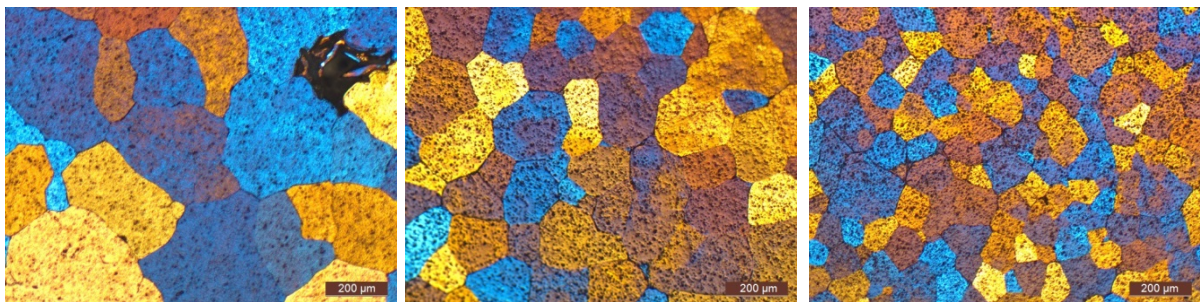


(a) No UST

(b) UST stop at 700°C

(c) UST stop at 660°C

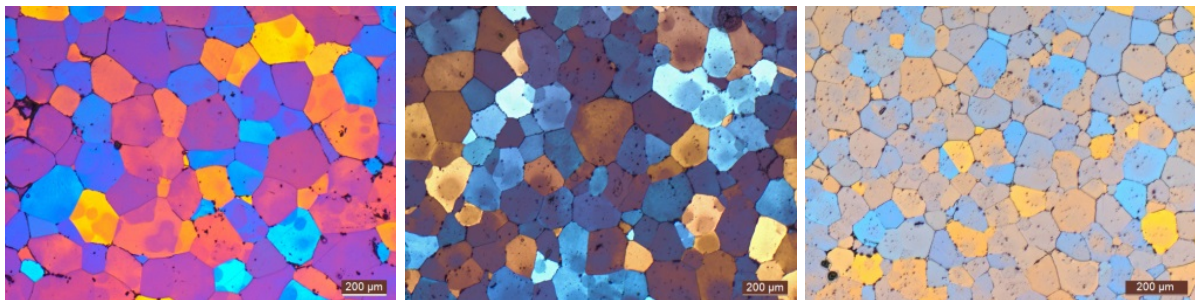
Fig. 1. Macrostructure of 50 ppm titanium addition with (a) no UST, and with UST which was stopped at temperatures of (b) 700°C and (c) 660°C.



(a)

(b)

(c)



(d)

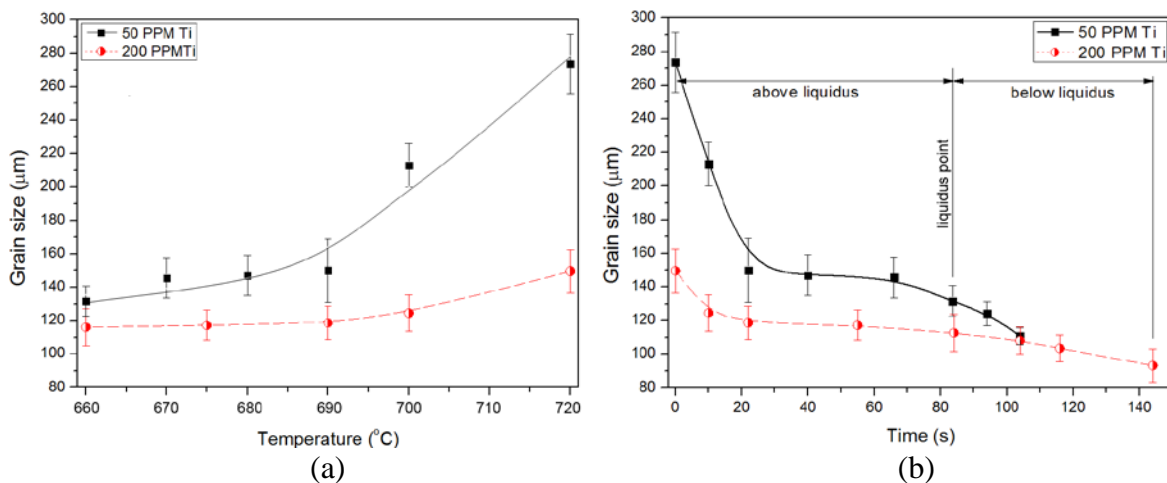
(e)

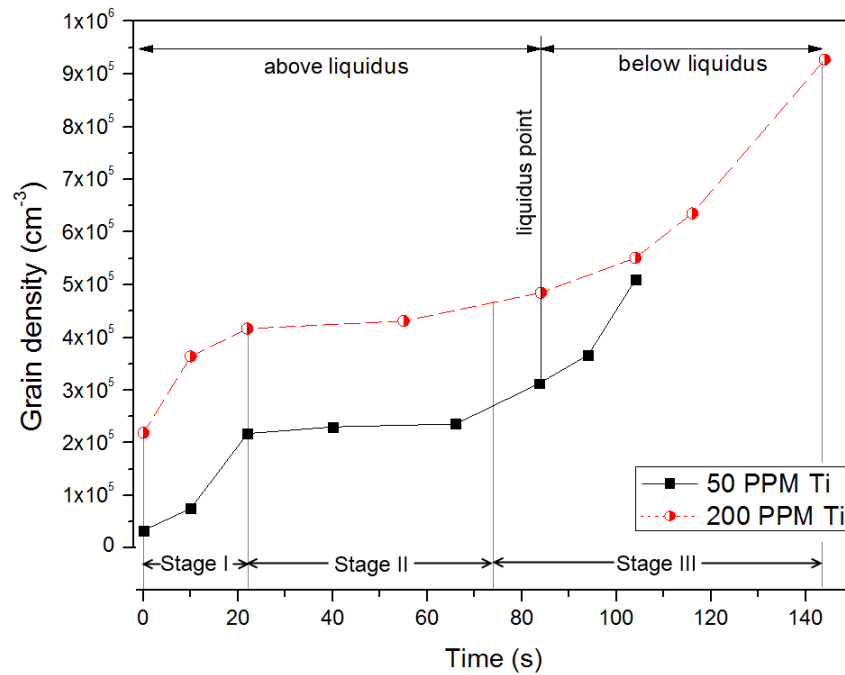
(f)

Fig. 2. Microstructure of 50 ppm (a, b and c) and 200 ppm (d, e and f) Ti additions with (a,d) no UST, and with UST stopped at temperatures of (b,e) 700°C and (c,f) 660°C.

Figure 3(a) shows the effect of the temperature at which the application of UST is terminated and Figure 3(b) the duration of the application of UST on the grain size of the samples

containing 50 and 200 ppm Ti. Applying UST until 690°C reduced the grain size considerably but the grain size did not significantly change from 690°C until just above the liquidus temperature. Figure 3(b) shows that during the first ~20 s of treatment, the grain size was reduced from $278 \pm 20 \mu\text{m}$ to approximately $150 \pm 20 \mu\text{m}$ and $120 \pm 10 \mu\text{m}$, respectively. A further increase in the time of UST application from 20 seconds to about 70 seconds resulted in minimal change in grain size. Finally, approaching the liquidus, the grain size started to decrease again with increasing UST time during the solidification stage. The application of UST to the 200 ppm Ti addition samples shows a similar trend in grain size against treatment time, but the level of grain size reduction for 200 ppm Ti from 145 to 115 μm is not as significant as for the 50 ppm Ti addition.





(c)

Fig. 3. The relationships between grain size and (a) the temperature at which UST was terminated and (b) the duration of UST application. (c) The relationship between grain density and UST application duration. Note that the grain sizes at 720 °C in (a) and 0 s in (b) are the effect of grain refiner addition without the application of UST.

Discussion

Figure 3(c) converts grain size into grain density, which is directly related to the number of activated nucleant particles.^[16] From Figure 3(c), the relationship between the number of activated nucleant particles and ultrasonic treatment time clearly shows that there are three distinct stages for both 50 ppm Ti and 200 ppm Ti additions: stages I and II occur above the liquidus temperature and stage III from just above to below the liquidus temperature. Stage I corresponds to the first 20 seconds of UST where the grain density increases significantly, from 3.37×10^4 to $2.28 \times 10^5 \text{ cm}^{-3}$ for the 50 ppm Ti samples and from 2.19×10^5 to $4.17 \times 10^5 \text{ cm}^{-3}$ for the 200 ppm Ti samples. Over the same time, the temperature of the melt below the sonotrode is increasing towards the bulk melt temperature^[14] indicating that the application of

UST at any temperature above the liquidus temperature may improve the efficiency of the master alloy.

Stage II is a period where the grain density remains more or less constant for about 40 seconds.

In stage III, the grain density increases remarkably with increasing UST duration after the melt reaches the liquidus temperature. It needs to be noted that the temperature is measured by thermocouples placed some distance away from the cooler sonotrode surface. Therefore, the start of stage III will appear to be above the liquidus temperature as recorded by the thermocouple as shown in Figure 3(b). Interestingly, the difference in the grain densities of the 50 and 200 ppm Ti samples is more or less constant in stages I and II, but the difference in grain density between the two addition levels reduces during stage III until 110 s when the grain densities become equal.

During stage I, de-agglomeration of TiB_2 clusters or particles assembled in oxide films most likely occurs.^[11, 18] Improved wetting of the TiB_2 particles and insoluble inclusions by the melt may also occur.^[11, 13] If a particle is not well wetted with the liquid aluminium, the particle can still be activated due to the melt penetrating the surface defects of the particle. Because of the high capillary pressure within the surface defects, this melt can solidify above the liquidus temperature and remain solid.^[11] Hence, at the liquidus temperature, solidification can start on the pre-existing patches of solid aluminium.^[19]

The fact that no change in grain density occurs during stage II implies there is a limit to the amount of de-agglomeration and wetting that can occur. Once completed no further change in grain size will occur if UST is terminated above the liquidus temperature. Acoustic streaming assists the released particles to be distributed uniformly throughout the melt. Han et al^[20] investigated the effect of ultrasonics on the distribution of phases in remelted Al-5Ti-B

master alloy, and proposed that cavitation and acoustic streaming accelerate the dissolution of the coarse TiAl_3 phase leading to a uniform distribution of Ti solute and TiB_2 particles in the melt. The existence of stage II implies that the maximum refining performance at the end of stage I is achieved over a certain period of time whether the application of UST is isothermal or, as in this case, the temperature decreases during cooling. The constant difference in grain densities between the 50 and 200 ppm Ti samples against UST duration during stage II indicates that, for the same thermal conditions, the grain density is proportional to the amount of the TiB_2 particles added to the melt.

During stage III, acoustic streaming creates an environment that promotes nucleation on more TiB_2 particles by producing a flat temperature gradient in the melt^[14, 21] so that the nucleation-free zone that forms around each grain^[22] is effectively eliminated. Thus, the nucleated grains are able to survive remelting in the uniformly undercooled melt while being transported throughout the melt.^[6, 22] In addition, cavitation-induced dendrite fragmentation can occur.^[11, 23, 24] It is also possible that grains are generated by a continuous process of nucleation, growth and detachment of crystals from the radiating surface of the sonotrode.^[14] Once nucleation occurs by either or both of the above mechanisms on or near the sonotrode, the new grains are then swept into the melt by the high degree of convection caused by acoustic streaming.^[14]

When conducted below the liquidus temperature, UST approximately doubles the grain density of both the 50 and 200 ppm Ti samples although it takes about twice as long for the 200 ppm samples (70 s compared to 30 s, Figure 3(c)). This observation may be related to a larger freezing range for the 200 ppm Ti alloy according to the Al-Ti phase diagram (Figure 4). By comparing Figures 3(a, b and c) it can be observed that the increase in grain density during stage III is similar to that in stage I. However, the grain size does not decrease as

much during stage III due to the cube root relationship defined earlier between grain density and grain size.

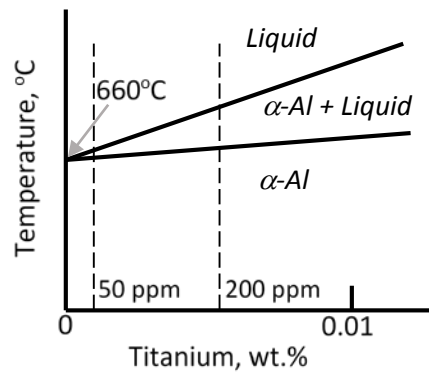


Fig. 4. The relevant section of the Al-Ti phase diagram highlighting the difference in freezing range between 50 and 200 ppm Ti alloys.

Two further observations can be made. Figure 3(a) shows that an addition of 200 ppm Ti without UST has a similar effect on grain size as applying UST to the 50 ppm Ti samples. On the other hand, after the application of UST for 110 s, Figures 3(b) and (c) show that UST decreases the grain size and increases the grain density of the 50 ppm Ti samples to that of the 200 ppm samples. This observation implies that the amount of grain refiner added becomes less significant in controlling the final grain size as the time of applying UST increases.

Conclusions

The combined application of UST and grain refiner reduces the grain size from large millimetre sized columnar grains formed without applying either treatment, to 278 μm with 50 ppm Ti and 150 μm with 200 ppm Ti grain refiner additions and down to 115 μm when combined with UST for 110 s.

Two distinct stages significantly enhance grain refinement while UST is applied:

- Stage I occurs well above the liquidus temperature where the efficiency of the refiner is improved possibly by de-agglomeration and wetting of TiB₂ particles, and their subsequent distribution throughout the melt by acoustic streaming. Stage I is followed by Stage II where little further improvement occurs.
- Stage III occurs at and below the liquidus temperature where nucleation of grains maybe enhanced by cavitation, which could also facilitate fragmentation and detachment of grains formed on the sonotrode. As well as transporting grains, acoustic streaming creates a uniformly undercooled temperature in the melt, which ensures the survival of these new grains producing a uniform fine grain size throughout the ingot.

After application of UST for 110 s the grain density and grain size of the 50 and 200 ppm alloys become equal indicating that the amount of master alloy can be reduced to 50 ppm without sacrificing grain size.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] J. Wannasin, R. Canyook, S. Wisutmethangoon, M.C. Flemings, *Acta Materialia*, **2013**, 61, 3897.
- [2] D.G. Eskin, *Materials Science Forum*, **2014**, 828-829, 112.
- [3] P.S. Mohanty, J.E. Gruzleski, *Acta Metallurgica et Materialia*, **1995**, 43, 2001.
- [4] A.L. Greer, A.M. Bunn, A. Tronche, P.V. Evans, D.J. Bristow, *Acta Materialia*, **2000**, 48, 2823.
- [5] M.A. Easton, D.H. StJohn, *Metallurgical and Materials Transactions A*, **1999**, 30–34, 1613.

- [6] D.H. StJohn, A. Prasad, M.A. Easton, and M. Qian, Metallurgical and Materials Transactions A., **2015**, 46, 4868.
- [7] S.V. Komarov, M. Kuwabara, O.V. Abramov. ISIJ International. **2005**, 45, 1765.
- [8] H.T. Li, Y. Wang, Z. Fan, Acta Materialia, **2012**, 60, 1528.
- [9] W.D. Wang, Y.C. Ma, B. Chen, M. Gao, K. Liu, Y.Y. Li. J. Materials Science and Technology, **2010**, 26, 639.
- [10] X.L. Liao, Q.J. Zhai, J. Luo, W.J. Chen, Y.Y. Gong. Acta Materialia, **2007**, 55, 3103.
- [11] G.I. Eskin, D.G. Eskin, Ultrasonic Treatment of Light Alloy Melts, 2nd Edition, CRC Press **2014**.
- [12] E.Q. Wang, G. Wang, M.S. Dargusch, M. Qian, D.G. Eskin and D.H. StJohn, IOP Conference Series: Materials Science and Engineering, **2016**, 117, 012050.
- [13] T.V. Atamanenko, D.G. Eskin, L. Zhang, and L. Katgerman, Metallurgical and Materials Transactions A, **2010**, 41, 2056.
- [14] G. Wang, M.S. Dargusch, M. Qian, D.G. Eskin, D.H. StJohn, Journal of Crystal Growth, **2014**, 408, 119.
- [15] M.A. Easton and D.H. StJohn, Materials Science and Engineering A, **2008**, 486, 8.
- [16] D. Liang, J. Sun, T. Liu, Q. Zhai, G Wang, D. H. StJohn, H. Dong and H. Zhong, Advanced Engineering Materials, **2015**, 17, 1465.
- [17] Y.H. Zhang, Y.H., D. Rübiger, & S. Eckert, Journal of Materials Science, **2016**, 51, 2153.
- [18] F. Wang, D. Eskin, J. Mi, T. Connolley, J. Lindsay, M. Mounib, Acta Materialia, **2016**, 116, 354.
- [19] D. G. Eskin, Materials Science and Technology, **2017**, 33, 636
- [20] Y. Han, K. Li, J. Wang, D. Shu, B. Sun, Materials Science and Engineering A, **2005**, 405, 306.

- [21] G. Wang, P. Croaker, M. Dargusch, D. McGuckin and D. StJohn, *Computational Materials Science*, 2017, 134, 116.
- [22] G. Wang, E.Q. Wang, A. Prasad, M. Dargusch, D.H. StJohn, *Shape Casting: 6th International Symposium*, Ed. M. Tiryakioglu, M. Jolly, and G. Byczynski, TMS (The Minerals, Metals & Materials Society), **2016**, 143.
- [23] H.L. Zhang, Y.F. Han, W. Zhou, Y.B. Dai, J. Wang, and B.D. Sun, *Applied Physics Letters*, **2015**, 106, 041606.
- [24] O.V. Abramov, *Ultrasound in Liquid and Solid Metals*, CRC Press, Boca Raton, FL, **1994**.