

PROCESSING OF METAL MATRIX COMPOSITES UNDER EXTERNAL FIELDS AND THEIR APPLICATION AS GRAIN REFINER

E. Djan, S. Vadakke Madam, N. Hari Babu, J. Tamayo-Ariztondo, D.G. Eskin, Z. Fan
The EPSRC Centre – LiME, BCAST, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

Keywords: Al–Mg–Ti /TiB₂ Composite, Grain Refinement, Mechanical Stirring, Ultrasonication

Abstract

In an attempt to develop an efficient grain refiner by application of external fields, aluminium-based metal matrix composite Al–Mg–Ti/TiB₂, has been processed by mechanical stirring and treated by external field such as ultrasonication. In this study we present the microstructural features of the composite and the grain structure of Al–Mg–Ti alloy when this composite is added as a master alloy. Preliminary tests with the addition of Al–3% Mg–0.01% Ti/TiB₂ master alloys to Al–3% Mg–0.01% Ti showed indication of grain refinement and improvement in Brinell hardness.

Introduction

Over the past century grain refinement by inoculation has shown significant improvement in mechanical and metallurgical properties of aluminum alloys as it produces a fine and equiaxed grain structure and it reduces defects such as porosity, ingot cracking, hot tearing, and the tendency of micro-segregation and scale of micro-segregation. It also eliminates the detrimental effects that a twinned, columnar, coarse, and non equiaxed grain structure poses to engineering application [1, 2].

Several agitation techniques have been used in the past to grain refine aluminum alloys during solidification such as mechanical stirring, shearing, ultrasonication, and electromagnetic stirring. However, these methods have limitations and very few are employed in industry so grain refinement is generally done commercially by inoculation (chemical addition to the melt) [3, 4].

Grain refinement by inoculation is achieved by addition of master alloys in the form of rods, waffles and nuggets. Currently grain refinement is achieved using various master alloys such as Al–Ti–B, Al–Ti–C, Al–Ti, Al–Zr and Al–Cr [1–5]. However, the most efficient grain refiners for aluminum alloys are Al₅Ti₁B and Al₃Ti₁B.

The presence of large Al₃Ti and AlB₂ particle agglomerates in Al–Ti–B master alloys limits down-stream processability of aluminum ingots, especially in manufacturing thin sheets and foils. The presence of large clusters of TiB₂ causes porosity in foils, defects in lithographic sheets and reduces mechanical properties. As a result, Al–Ti–B grain refiners have limited use in alloys for aerospace industries [11].

Despite considerable research done in the production and optimization of an Al–5% Ti–1% B grain refiner over the past three decades, the problems associated with TiB₂ agglomeration, large Al₃Ti particles and impurities from KF–AlF₃ flux still exist and therefore there is a need for a novel and efficient grain refiner to be developed [3, 6–10].

Addition of Al₅Ti₁B rod to an AA1050-type alloy produces a grain size typically between 150 μm and 200 μm but the ingots are huge (1.5×1×10 m). To produce very thin sheets such as kitchen foils these ingots have to be thermo-mechanically

processed to obtain 40–60 μm thick aluminum foil. To produce such thin foils, the aluminum ingot should be free from TiB₂ clusters and larger Al₃Ti.

In modern practice, the manufacture of Al–Ti–B master alloys involves a reaction between potassium hexafluorotitanate (K₂TiF₆) and potassium tetrafluoroborate (KBF₄). The by-products of this reaction can have negative environmental effect.

The reaction of K₂TiF₆ and KBF₄ in aluminum requires larger volumes of KBF₄–K₂TiF₆ (370kg/1Tonne) and a generation of fluoride emissions which leads to expensive emission control systems [11].

In this paper, we utilize external field methods such as mechanical stirring and ultrasonication to process Al–Mg–Ti/TiB₂ composite using synthetic TiB₂ particles and show that this composite is capable of grain refining aluminum alloy and contributes to improved hardness.

Experimental Procedure

Al–Mg–Ti alloy preparation

A 10 kg aluminum ingot with commercial purity 99.8% was heated and melted at temperature of 750 °C in an electrical resistance furnace (Carbolite) using a clay graphite crucible. Nitrogen bearing gas was introduced onto the surface of the melt after the dross has been removed to avoid oxidation after addition of magnesium. Magnesium content below 5 wt% was introduced into the molten aluminum using commercial purity magnesium ingot wrapped and pre-heated in aluminum foil at a temperature of 150 °C via a plunger until dissolution into the molten aluminum. An Al–6% Ti master alloy was then added to the melt in a hypoperitectic concentration (about 0.01% Ti). The resultant alloy was then cast into a steel mould which has been pre-heated at 250 °C, and allowed to solidify at room temperature.

Preparation of Al–3% Mg–0.01Ti/TiB₂ composite

Mixing of particles: In an attempt to understand particle distribution in the composite, 800 g of the Al–Mg–Ti master alloy was re-melted in an electrical resistance furnace, and 2 wt% of synthetic TiB₂ particles (<10 μm in size) supplied by Sigma Aldrich were introduced using an impeller. Before being introduced into the melt, the particles were pre-heated at 200 °C in an oven for 4 hours to remove moisture from the particles.

The melt was kept at 650 °C in an electrical resistance furnace and the particles were introduced into the melt in the furnace using a spatula whilst being mechanically stirred with four blade steel impeller with the torque produced by an IKA EUROSTRA 60 digital motor at a velocity of 600 rpm for 4 minutes. Before stirring, the steel impeller was pre-heated at 200 °C and impeller blades were twisted at a swift angle of 30 degrees to increase the lift and reduce drag caused by high viscosity of the melt as a result of addition of TiB₂ particles thus improving the efficiency

of the stirring. The molten Al–Mg–Ti/TiB₂ slurry was heated and held in the furnace for 40 minutes to reach a temperature of 760 °C for further treatment using external fields such as ultrasound.

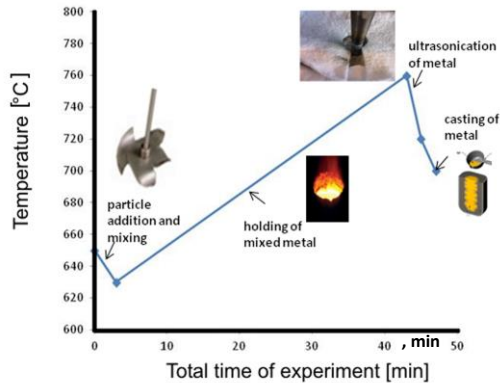


Figure 1. Schematic illustration of particle introduction into melt and ultrasonification.

Ultrasonic treatment of the slurry prior to casting: To ensure uniform distribution of TiB₂ particles, and reduce segregation of these particles, a water-cooled ultrasonic magnetostrictive transducer working at a frequency of 17.3 kHz and with the maximum power between 4 and 5 kW was used to apply ultrasonic vibrations in the cavitations regime and acoustic streams to the melt using a Nb conical horn pre-heated at 680 °C. To enhance particle dispersion, the ultrasonication was carried out for 5 minutes. The melt temperature dropped from 760 °C to 700 °C during ultrasonication as a result of melt exposure to air and some heat-sink effect from the massive horn. The melt was then taken out of the furnace and allowed to solidify in the crucible. The principle scheme of experiment is shown in Fig. 1.

Structure analysis and hardness measurement

As cast samples solidified in the crucible were cut and ground using silicon carbide abrasives via standard metallographic techniques. The samples were further polished using a polishing cloth sprayed with OPS solution. Figure 2 shows the sections where samples were taken for metallography. The volume fraction of particles was then measured from sectioned samples at locations 1 through 5.

The volume fraction of particle was measured by the systematic manual point method. In this method, an array of points formed by a grid were superimposed on the micrographs taken from sections 1 – 5 and the number of points were counted and averaged for a selected number of fields and expressed as a percentage. Statistical analysis of the data was performed.

To check the grain refinement efficiency of the Al–3% Mg–0.01% Ti / 2 wt% TiB₂ composite grain refiner, 1 wt% of the composite was added to 500 g melt of the Al–3% Mg–0.01% Ti alloy at 750 °C. The melt was stirred rigorously for 15 minutes after addition, and allowed to solidify in the crucible at room temperature. During solidification, thermocouples were inserted into the melt to record the cooling curve of the alloy. The samples were cut, polished and etched with Tucker’s etchant (45 ml HCl, 15 ml HNO₃, 15 ml HF and 25 ml H₂O).

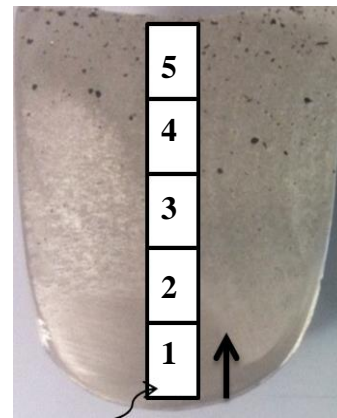


Figure 2. Cross-section of a composite casting solidified in a crucible. Labels 1, 2, 3, 4 and 5 represent location of sections cut for metallographic preparation.

Further experiments were conducted to check the potency of the TiB₂ containing composite refiner after ultrasonication. Hardness tests were conducted after milling the surface and grinding by a standard emery paper 1200 grit size. The samples were clamped and tested by a Brinell Hardness Tester BH3000, using application time 5 s, dwell time 15 s with a 10 mm indenter. The average data are reported with the 5% measurement accuracy.

Results and Discussion

Distribution of TiB₂ particles in Al - 3Mg - 0.01Ti/TiB₂

Figure 3 shows optical micrographs of the composites (a) for a sample produced with only mechanical stirring and (b) for an ultrasound treated sample. The microstructures were taken at location 3 as depicted in Fig. 2. In conventional mixing process, TiB₂ particles (dark in contrast) are shown to form agglomerates that are accumulated at the Al grain boundaries. These agglomerates can be effectively dispersed, as shown in Fig. 3(b), after ultrasonic treatment prior to casting.

The observed uniform distribution of TiB₂ particles in the Al matrix after ultrasonic treatment could be due to cavitations and acoustic streams created in the melt during ultrasonication which disperses agglomerates of TiB₂ particles leading to uniform distribution in the melt [4, 8, 14].

Figure 4 shows the spatial variation of the measured volume fraction for sectioned samples from locations 1–5 in Fig. 2.

From Figure 4, the volume fraction of particles increases from the bottom (Section 1, Fig. 2) of the sample to the middle (Section 3, Fig. 2) and then decreases in the case of ultrasonic processing. Volume fraction measurements taken from the sample prepared using mechanical stirring shows a decrease in number of particles from the bottom to the top of the melt as compared to ultrasonication. During ultrasonication, acoustic streams could pull settled TiB₂ particles from the bottom of the crucible to the middle of the melt leading to an increase in volume fraction in the middle of the sample (Section 3). As a result, a better distribution of TiB₂ particles throughout the sample was observed after solidification.

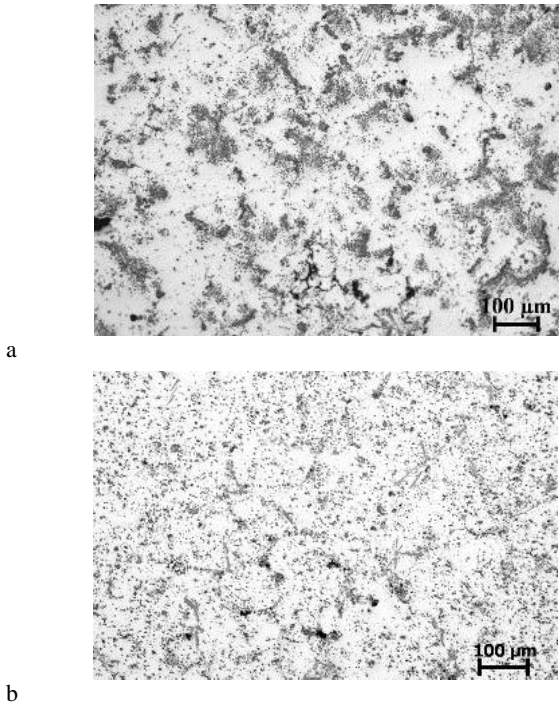


Figure 3. Dispersion of 2 wt% TiB_2 particles in Al-Mg-Ti composite: (a) prepared using mechanical stirring; (b) prepared using mechanical stirring with ultrasonication.

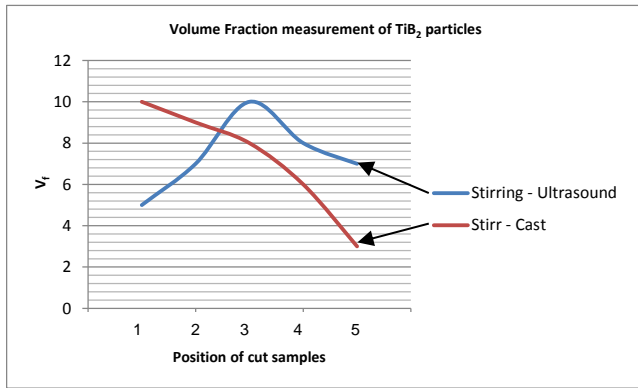


Figure 4. Measured volume fraction of TiB_2 particle for samples taken from Sections 1–5 in Fig. 2.

Brinell hardness results

Figure 5 shows results for hardness tests conducted on the matrix alloy and the TiB_2 containing composites produced by mechanical stirring and by ultrasonication. The hardness of the alloys increases from 44 HB for the matrix alloy to 47 HB after particles were introduced by mechanical stirring and further to 50 HB after ultrasonication, as a result of better dispersion of particles. Microstructural observations in mechanically stirred samples reveal that the agglomerates contain porosity. In the ultrasonication process, no such agglomerates with porosity were observed. This may contribute to the hardness increase. This result agrees with previous research showing that ultrasonication

leads to improvement in mechanical properties such as hardness in alloys [13].

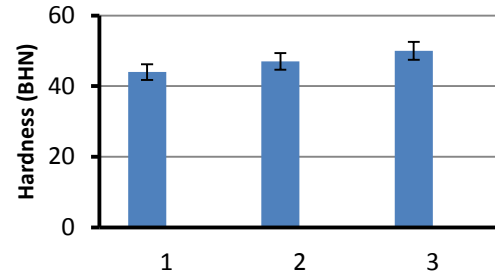


Figure 5. Hardness values for Al-3% Mg-0.01% Ti alloy (1); Al-3% Mg-0.01% Ti/ TiB_2 composite after mechanical mixing (2), and Al-3% Mg-0.01% Ti/ TiB_2 composite after ultrasonication (3).

Grain refinement using Al-3% Mg-1% Ti/TiB_2 master alloy

Figure 6 shows grain refinement effect associated with addition of the prepared master alloys. The etched specimens solidified in the crucible (for a slow cooling effect) showed coarse grains in the matrix alloy as compared to the samples with 1 wt% addition of TiB_2 composite grain refiner.

There is a noticeable grain refining effect associated with introduction of the composite master alloy, which is further enhanced by ultrasonic melt processing. These effects can be expected and agree well with reference data [1, 4, 7, 8, 12, 14].

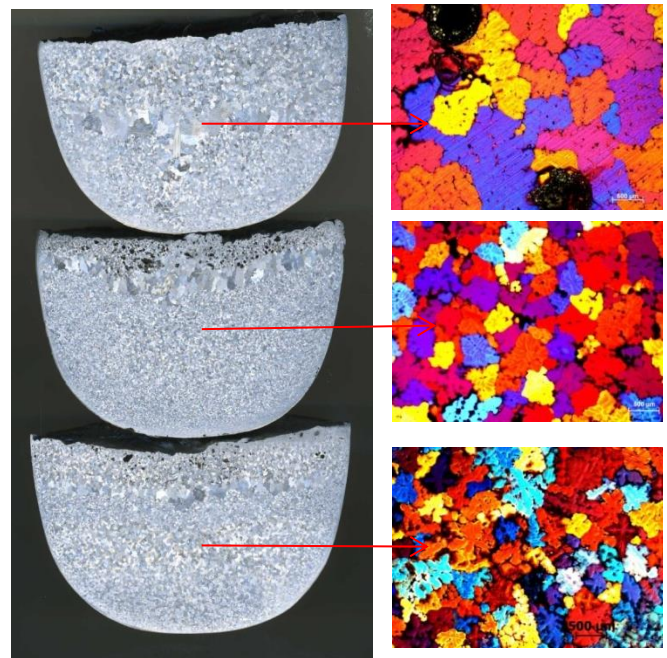


Figure 6. Grain refinement effect of an Al-Mg-Ti/ TiB_2 composite master alloy (1%) added to an Al-3% Mg-0.01% Ti alloy; top: no additions, middle: addition of a master alloy made using mechanical stirring and bottom: addition of a master alloy prepared using ultrasonication.

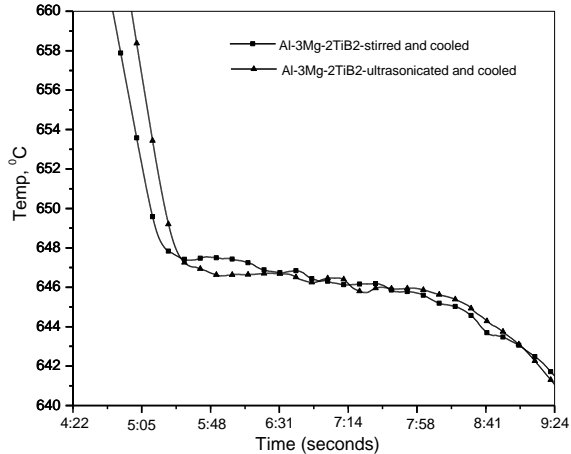


Figure 7. Cooling curves of Al-3% Mg-0.01% Ti alloy with the addition of TiB₂ from composites prepared using stirring or stirring and ultrasound.

Figure 7 shows measured cooling curves after grain refiner addition produced using mechanical stirring and ultrasonication processes. Cooling rates are similar in both curves suggesting that cooling conditions during solidification in both samples are the same. In both cases, it could be observed that undercooling is negligible (<0.1 K) and no noticeable recalescence took place. This suggests that 1 wt% addition of Al-Mg-Ti-2 wt% TiB₂ composite to the base alloy resulted in enhanced heterogeneous nucleation.

The observed grain refining effect, however, is less than could be expected from addition of TiB₂ particles. This might be due to low cooling rate that did not allow smaller particles to be activated as nucleating substrates [1, 5].

Summary

- Application of external fields such as ultrasonication aids good dispersion of TiB₂ particles in an Al-Mg-Ti alloy as compared to mechanical stirring.
- Ultrasonication after addition of TiB₂ particles into the matrix leads to improved particle dispersion, thus affecting mechanical properties such as hardness of the alloy.
- An Al-3% Mg-0.01% Ti-2% TiB₂ composite master alloy showed indication of grain refinement due to the presence of TiB₂.
- Further work will be aimed at improving the efficiency of these particles in grain refinement by increasing the cooling rate in solidification and optimizing the process parameters of particles introduction and distribution in the matrix.

Acknowledgement

The authors wish to acknowledge financial support from the ExoMet Project, which is co-funded by the European Commission in the 7th Framework Programme (contract FP7-NMP3-LA-2012-280421), by the European Space Agency and by the individual partner organizations.

References

- Quested, T.E. (2004) "Understanding mechanisms of grain refinement of aluminium alloys by inoculation", *Materials Science & Technology*, vol. 20, no. 11, pp. 1357-1369.
- Li, H.-T., Wang, Y. and Fan, Z. (2012) "Mechanisms of enhanced heterogeneous nucleation during solidification in binary Al-Mg alloys", *Acta Materialia*, vol. 60, no. 4, pp. 1528-1537.
- McCartney, D.G. (1989) "Grain refining of aluminium and its alloys using inoculants", *International Materials Reviews*, vol. 34, no. 5, pp. 247-260.
- Hari Babu N., Fan Z., and Eskin D.G. (2013) "Application of external fields to technology of metal-matrix composite materials" *TMS 2013 Annual Meeting Supplemental Proceedings*, Warrendale, TMS/Wiley, 2013, p 1037-1044.
- StJohn, D.H. et al. (2013) "A Brief History of Grain Refinement of Cast Light Alloys", *Materials Science Forum*, vol. 765, pp123-129 (Trans Tech Publication, Switzerland).
- McKay, B.J., Nunner, G., Geier, G.F. and Schumacher, P. (2009) "Impurities in Al-5Ti-1B grain refiner rod", *International Journal of Cast Metals Research*, vol. 22, no. 1-4, pp. 212-215.
- Mohanty, P.S. and Gruzleski, J.E. (1995) "Mechanism of grain refinement in aluminium", *Acta Metallurgica et Materialia*, vol. 43, no. 5, pp. 2001-2012.
- Han, Y., Shu, D., Wang, J. and Sun, B. (2006) "Microstructure and grain refining performance of Al-5Ti-1B master alloy prepared under high-intensity ultrasound", *Materials Science and Engineering A*, vol. 430, no. 1-2, pp. 326-331.
- Zhang, X., Ren, Y. and Sun, Z. (2006) "Study on Grain Refining and Metamorphism of ZL111 Aluminium Alloys", *Journal of China University of Mining and Technology*, vol. 16, no. 4, pp. 475-479.
- Limmaneevichitr, C. and Eighed, W. (2003) "Fading mechanism of grain refinement of aluminum-silicon alloy with Al-Ti-B grain refiners", *Materials Science and Engineering A*, vol. 349, no. 1-2, pp. 197-206.
- Birol, Y. (2007) "Production of Al-Ti-B master alloys from Ti sponge and KBF₄", *Journal of Alloys and Compounds*, vol. 440, no. 1-2, pp. 108-112.
- Han, Y., Li, K., Wang, J., Shu, D. and Sun, B. (2005) "Influence of high-intensity ultrasound on grain refining performance of Al-5Ti-1B master alloy on aluminium", *Materials Science and Engineering A*, vol. 405, no. 1-2, pp. 306-312.
- Yao, L., Hao, H., Ji, S., Fang, C. and Zhang, X. (2011) "Effects of ultrasonic vibration on solidification structure and properties of Mg-8Li-3Al alloy", *Transactions of Nonferrous Metals Society of China*, vol. 21, no. 6, pp. 1241-1246.
- Estruga, M., Chen, L., Choi, H., Li, X. and Jin, S. (2013) "Ultrasonic-assisted synthesis of surface-clean TiB₂ nanoparticles and their improved dispersion and capture in Al-matrix nanocomposites", *ACS Applied Materials and Interfaces*, vol. 5, no. 17, pp. 8813-8819.

