

Improvement of mechanical properties of Al-Si alloys using an in-situ integrated Al₂TiB-Mg refiner

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Abstract: In order to improve the effectiveness and stability AlTiB grain refiners for cast Al-Si alloys, the present study investigated the grain refinement of cast Al-Si alloys using an in-situ integrated Al₂TiB-MgAl₂O₃ (Al₃TiB₂-MgAl₂O₃) master alloy, which was synthesised through a two-step chemical reactions to create TiB₂ particles and magnesium aluminate (MgAl₂O₃) phase in the master alloy. Experimental results showed that the fine equiaxed grains were obtained in an A356 alloy treated with Al₂TiB-MgAl₂O₃ master alloy. In comparison with the α -Al grain size at a level of 950 μm in the A356 alloy without using any grain refinement, the conventional Al₅Ti₁B could refine to 620 μm and, Al₂TiB-MgAl₂O₃ could refine to 290 μm for the α -Al grains in the same A356 alloy. The yield strength, ultimate tensile strength and elongation of the A356 alloy refined by Al₂TiB-S was 256.6MPa, 313.0MPa and 7.8% respectively, which was increased by 6% (13.8MPa), 3%(8.3MPa), and 13% (1.0%) in comparison with that obtained by Al₅Ti₁B. The significant improvement of mechanical properties was attributed to the effective nucleation of α -Al phase and the double-peak size distribution of eutectic Si phase in the A356 alloy treated by Al₂TiB-S. The formation of MgAl₂O₄ layer on the TiB₂ surface is expected to reduce the misfits and promote the nucleation and therefore improving the effectiveness of grain refinement.

Keywords: Aluminium alloys; Microstructure; Grain refinement; Mechanical properties; Nucleation

1. Introduction

Grain refinement by adding master alloys containing inoculant particles has been a common manufacturing practice over decades for most commercial aluminium alloys because the refined microstructure reduces casting defects, increases castability and thus improves the mechanical properties of as-cast components [1,¹]. The most popular grain refiners are based on Al-Ti-B master alloys [²,³], which can be generally divided into two groups: TiB₂ with excessive Ti and TiB₂ with excessive B.

The representative system of TiB₂ with excessive Ti is Al₅Ti₁B [⁴], which usually contains 3.2wt.% TiB₂, 2.8wt.% Al₃Ti and balanced Al. Al₅Ti₁B has been the dominant grain refiner for aluminium and aluminium alloys since its first application in 1960's [2,3]. It has been identified that the addition of Al₅Ti₁B master alloy at a level of 0.2wt.% of total weight of melt can achieve best refinement [5]. Extra addition is not necessary and can not improve the refinement [6]. However, TiB₂ particles are still not recognised as the most effective nuclei for α -Al due to the large misfit between TiB₂ and Al [7]. It is generally agreed that the Al₃Ti in Al₅Ti₁B master alloy is instantly melted in aluminium melt and existed in the form of free Ti to supply constitutional undercooling during grain growth [8,⁹], and a mono-layer of Al₃Ti is formed on the TiB₂ surface to decrease the TiB₂/Al misfit and to activate TiB₂ particles as effective nuclei for α -Al phase [¹⁰,11]. However, Al₅Ti₁B master alloy is not very effective in the aluminium alloys containing specific elements. For example, the excessive Si could deteriorate the grain refinement of Al₅Ti₁B in cast Al-Si alloys [5,6]. The grain size increases with increasing the Si content at a level of higher than 3wt.%. Therefore, the application of Al₅Ti₁B could not obtain significant grain refinement in cast Al-Si alloys, although it is still popular in industry as a common grain refiner. Other master alloys in this group include Al₅Ti_{0.2}B [¹²], Al₃Ti₁B [¹³]
(need to check the details) and Al₆Ti [¹⁴], which were all designed by controlling the amount of excessive Ti in the master alloys.

On the other hand, the alternative master alloys containing TiB₂ with extra B include Al₁₁Ti₃B [¹⁵], Al₁₁Ti₅B [¹⁶], Al₃Ti₃B [7], and Al_{2.5}Ti_{2.5}B [17]. It was reported that

the excessive B in AlTiB grain refiners is able to offer better grain refinement than Al₅Ti₁B for cast Al-Si alloys [8,9], indicating B-rich AlTiB is more effective than Al₅Ti₁B as grain refiners for cast Al-Si alloys. The refinement mechanism has been identified that the excessive boron is segregated at the TiB₂/Al interface and forms a boron-rich layer to undergo a eutectic reaction and to nucleate α -Al phase at a temperature above the liquidus temperature of aluminum alloys [10,18]. However, one of the major problems associated with these grain refiners is their stability because the transformation of AlB₂ to TiB₂ is unavoidable during refinement process [8,9]. The fading of grain refinement is relatively quick and the melt with refiners must be cast within a short period of time, usually within 15min (??).

In fact, AlTiB master alloys contain TiB₂ only (weight ratio Ti:B=2.2:1) without excessive Ti and/or B has rarely been used as grain refiner (need to check). The main reason is that the misfits between TiB₂ and Al is too large to nucleate Al on the surface of TiB₂ solid particles. In order to improve the refinement effectiveness and stability of grain refinement of AlTiB based refiners for cast Al-Si alloys, several attempts have been carried out in recent years. One progress was that spinel (MgAl₂O₄) phase has a small misfit with TiB₂ and Al, which can possibly nucleate Al under appropriate conditions [19]. Although the spinel (MgAl₂O₄) was expected to be able to increase the stability of grain refinement, the generation of spinel (MgAl₂O₄) was not easily controlled. More importantly, it was not easy to distribute spinel throughout the melt as the oxidation is always from the melt surface and there is lack of carriers to disperse spinel (MgAl₂O₄) in the melt. It was anticipated that these problems can be overcome if introducing foreign carriers for enhancing the distribution of spinel phase and promoting the grain refinement. TiB₂ is the first option for these purposes.

Therefore, the present research aims to investigate the combined effect of Al_{2.2}Ti₁B and MgAl₂O₄ master alloy on the grain refinement of an A356 Al-Si alloy, in which the TiB₂ particles were used as the carriers for spinel (MgAl₂O₄) and the spinel (MgAl₂O₄) phase were used to reduce the misfit between TiB₂ and Al. The

effectiveness of Al_{2.2}Ti₁B with MgAl₂O₄ grain refiner was comparably evaluated in association with Al₅Ti₁B, Al₃Ti₃B and no grain refinement. The grain refinement with prolonged effective time after inoculation (fading characteristics) was also studied for the different grain refiners in the cast A356 Al-Si alloy. The discussion is focused on the possible mechanism of grain refinement.

2. Synthesis and analysis of Al_{2.2}Ti₁B- MgAl₂O₃ master alloy

The master alloy of new grain refiner was synthesised by chemical reactions. The synthesis process consisted of two steps: the synthesis of TiB₂ particles and the creation of magnesium aluminate spinel phase. The synthesis of TiB₂ particles was achieved by salt reactions among molten Al, K₂TiF₆ and KBF₄ at the stoichiometry ratio of Ti and B at 850°C for 30 minutes, in which the amount of TiB₂ particles was controlled at a level of 3wt.% in aluminium melt [11,12]. The creation of magnesium aluminate spinel phases was obtained by adding pure Mg into the melt made in the previous step to react with oxygen and aluminium by holding the mixture at 700±5°C for 4 hours to form MgAl₂O₄ phase in the aluminium melt [13]. The flux and by products in the first step reaction was removed from the furnace before adding pure magnesium into the melt for the second step reaction. Once finishing the synthesis, the melt was subjected for a degassing and slag removal. The ingots of master alloy were subsequently made at a size at 130mm long with a square cross section of 15x15mm. The master alloy was analyzed by ICP-AES and the composition was 2.2wt%Ti, 1wt.%B, 0.4wt.%Mg, and balanced by Al and unavoidable impurity elements at trace levels. The amount of TiB₂ particles in the master alloy was thus to be 3.2wt.% (??) according to the molar calculation. This master alloy was defined as Al_{2.2}Ti₁B-S hereafter.

In order to confirm the phase formation in the master alloy of new grain refiner, XRD analysis was carried out for Al_{2.2}Ti₁B-S together with the commercial Al₅Ti₁B and Al_{2.5}Ti_{2.5}B. The results are shown in Figure 1, in which TiB₂, Al₃Ti (?) and Al were found in the Al₅Ti₁B master alloy, but TiB₂, B₂Al(??) and Al were found in the

Al_{2.5}Ti_{2.5}B master alloy. In the Al_{2.2}Ti₁B-S master alloy, only TiB₂ and Al were clearly shown in the XRD pattern, but Mg and O were not clearly observed. Only a trace amount of O was seen in the XRD pattern. Also, the MgAl₂O₄ phase (spinel) was not detected in the Al_{2.2}Ti₁B-S master alloy possibly because the limited content was below the tolerance of diffractor instrument. In order to further confirm the formation of MgAl₂O₄ (spinel) phase. The master alloys were further examined by SEM. The morphology, size and distribution of TiB₂ particles are shown in Figure 2. It was confirmed that the sizes of TiB₂ particles were in a range of ** to ** and the average was 1µm for all of these three master alloys. Morphology and distribution of TiB₂ particles were similar in the three master alloys. The previous results [11] have confirmed that this type of distribution of TiB₂ particles was able of ensuring the particles as the potency substrates of α-Al nucleation [14]. However, the results in Figure 2 confirmed that free Ti was detected in the Al₅Ti₁B master alloy, but no free Ti was found in the Al_{2.5}Ti_{2.5}B and Al_{2.2}Ti₁B-S master alloys. The analysis of the TiB₂ particle composition is shown in Table 2. It was confirmed the existence of Mg and O in association with TiB₂ particles in the Al_{2.2}Ti₁B-S master alloy, whereas there was no Mg and O in the Al₅Ti₁B and Al_{2.5}Ti_{2.5}B master alloy. Although the previous study has shown that the existence of Mg in aluminium melt promoted to the formation of MgAl₂O₄ when the melt was held for sufficient reaction time [13], it is not very sure whether there was any MgAl₂O₄ phase in the synthesised master alloy. In order to clarify the existance of spinel, , the melt of Al_{2.2}Ti₁B-S master alloys were filtered using the commerially availabe ** to condense the melt and the residues on the filter would have much more TiB₂ particles and associated oxide phase, therefore it could be used to examine the phase formation. Figure 3 is the SEM images to show the morphology of of TiB₂ and associated MgAl₂O₄ phase, which was identified by SEM/EDS. By combining the results shwon in Figures 1, 2 and Table 2, it was confident to claim that a spinel phase was formed in the Al_{2.2}Ti₁B-S master alloy.

3. Experimental

A356 alloy (Norton Aluminium, UK) was used to assess the grain refinement in the

present study. During experiments, the A356 alloy was melted in a graphite-grey crucible in a furnace at 750°C. After one hour of homogenization at 750°C, the melt was subjected to degassing, during which argon was introduced into the melt by a commercial rotatory degasser at 500 rpm for 3 minutes and the top surface of the melt was covered by commercial granular flux. Then, 0.01wt.% of Al-10wt.%Sr master alloy (LSM, UK) was added into the melt to modify the eutectic Si. The melt was subsequently homogenized in the furnace at 725°C for 30 minutes. After skimming, 0.2wt.% of the master alloys was added into the melt, during which the different grain refiners were separately used and each time only used one type of grain refiner. After that, slow stirring by a rod was applied to disperse refiner into the melt. The slow stirring was continued for extra 30 seconds after the added refining master alloy was completely disappeared in the melt. The melt was then held for 30 minutes in the furnace. After that, the melt was poured into a TP-1 mould to make casting for grain refinement assessment and composition analysis. The composition of A356 alloys using different grain refiners were shown in Table 2, which were pretty close each other. In the meantime, tensile test samples were made using a ASTM standard mould (ASTM B557-15), which was preheated to 300°C before being used for casting. It need to emphasis that the melting and casting experiments were conducted with the exactly same procedure to maintain the minimum error.

The microstructural refinement was examined using TP-1 samples. The samples used for grain size analysis were also cut from the center of tensile test bar and were anodized by 4% HBF₄ water solution for 1 minute at 20V. The microstructural examinations were carried out using a Zeiss optical microscopy, which was equipped with digital image analysis system and a field-emission scanning electron microscopy (FE-SEM, SUPRA 35VP, Carl-Zeiss Company) equipped with an energy dispersive X-ray spectroscopy (EDS) and high resolution transmission electron microscopy (HR-TEM, JEOL 2100F). A D8 advanced Bruker X-ray diffractometer with CuK α radiation was employed for phase confirmation. The reported data was the average of at least five points/areas analyzed in the samples.

The samples for tensile properties test were subjected to a T6 heat treatment, in which the samples were solutionised at 540°C for 8 hours and immediately quenched into cold water, followed by an ageing at 170°C for 8 hours. The electric resistance furnace for T6 heat treatment was preheated to a given temperature and maintained the temperature consistently for at least one hour before starting to put samples into the furnace chamber for heat treatment. Universal Electromechanical Testing System equipped with Bluehill controls software and a ± 50 kN load cell. All tensile tests were performed at an ambient temperature (about 20°C). The gauge length of the extensometer was 50 mm and the ramp rate for extension was 1mm/min. Each set of data reported was based on the properties obtained from 5 to 8 samples.

4. Results and discussion

Figure 4 shows the refinement results of TP-1 casting sample made by A356 alloys treated with different grain refiners. It can be seen that the average grain size was 950 μm in the A356 alloy when no grain refiner was added before casting. However, the average grain size was 620 μm and ** for the A356 alloys refined by Al5Ti1B and Al2.5Ti2.5B master alloys, respectively. Moreover, the average grain size was refined to 290 μm for the A356 alloy treated by Al2.2Ti1B-S master alloy. These confirmed that both Al5Ti1B and Al2.5Ti2.5B master alloys, which reveal that both Ti-riched TiB₂ and B-riched TiB₂ could refine A356 alloys, although the grain refinement was not very effective. However, when comparing the refinement results, it is clear that the Al2.2Ti1B-S could generate finer microstructure than Al5Ti1B and Al2.5Ti2.5B, which implied that Al2.2Ti1B-S was more effective than Al5Ti1B and Al2.5Ti2.5B as grain refiner for A356 alloy.

The mechanism of α -Al grain refinement by adding Al5Ti1B was confirmed that an Al₃Ti atomic layer on the TiB₂ substrates could nucleate α -Al grains and the free Ti being departed from the solid/liquid interface could restrict the growth of α -Al phase [15]. Meanwhile, Ti and Si could form Al(TiSi) phase to consume Ti in the melt

of cast Al-Si alloys. This could reduce the total number of effective nuclei and therefore deteriorate the refinement effect of Al₅TiB. On the other hand, (add something why B-rich grain refiner not work well for Al-Si). In the present study, it was found no free Ti within the Al_{2.2}TiB-S grain refiner, only TiB₂ and MgAl₂O₄ phase were found after a long holding for the mixtured melt in the furnace [13]. The calculation results has shown the misfit between TiB₂ and Al is 4.2% [20], which results in that the TiB₂ particles were not effective nuclei for α -Al, but the TiB₂ particles could become effective after segragating a thin layre of Al₃Ti on the particle surface because the misfit between Al₃Ti and Al is only ** and the misfit between TiB₂ and Al₃Ti is **. To examine the Al_{2.2}TiB-S system in the similar way, the misfit between MgAl₂O₄ and Al was only 1.4%. Therefore, the MgAl₂O₄ particles formed by the oxidation of Al and Mg could be the substrate of nucleation, as observed in the experimental results. The small misfit might be the reason why Al_{2.2}TiB-S was more effective that Al₅TiB for the grain refinement of A356 alloy. From the refinement point of view, the neuclei size exceeding 1 μ m was not desirable because nucleation was supposed to be initiated from the large particles because only a small undercooling was needed for the nucleation of large nuclei [21]. Once the large particles were nucleated, the realease of latent heat would increase the local temperature in the melt and destory the undercooling at the solid/liquid interface of solidification. This would prevent the remain particles became effective nuclei for the subsequent nucleation. Therefore, it is desirable that sufficient nuclei could be formed during the first wave of nucleation, which required the potential culeai to have an appropriate size distribution and surface quality [22]. It was reported that the MgAl₂O₄ spinel is a stable compound in aluminum melt and the exceeding Ti and Mg could be segregated and affixed on TiB₂ particles in Al-TiB₂ system [11,12]. Therefore, there were several ways to combine TiB₂ particles and MgAl₂O₄ spinel phase together to form integrated system between TiB₂ particles and MgAl₂O₄ spinel phase. These are roughly described in Figure 5. MgAl₂O₄ phase could be varied from a small fraction of TiB₂ particles to a large fraction of TiB₂ particles. In one utmost case, it was expected to form a thin MgAl₂O₄ layer on TiB₂ paperticle in the master alloy for grian

refinement. Obviously it was unclear for how these two phase interaction and whether the thin layer was continuous or segmented because of the limit of instrumental capability.

In order to observe the $MgAl_2O_4$ phase on TiB_2 substrates in the $Al_{2.2}Ti_1B-S$ master alloy, the interface was examined by TEM with the selected area diffraction pattern (SADP). The results are shown in Figure 6. The SADP at the TiB_2/Al interface in the $Al_{2.2}Ti_1B-S$ master alloy revealed that the $MgAl_2O_4$ was indeed existed at the TiB_2/Al interface. The TiB_2 was likely the substrates to grow $MgAl_2O_4$ and the $MgAl_2O_4$ was further for growth of aluminium phase. It was also possibly to be another case, in which the TiB_2 was the substrates of $MgAl_2O_4$ and the $MgAl_2O_4$ to be the substrates of Al_3Ti and the Al_3Ti to be the substrate of $\alpha-Al$. The main reason was that the misfit between Al_3Ti and $MgAl_2O_4$ is **, which is smaller than the misfit between Al_3Ti and TiB_2 . Therefore, Al_3Ti is easier to grow up from $MgAl_2O_4$, rather than TiB_2 particles. Consequently, the $MgAl_2O_4$ might act as a bridge between TiB_2 and Al_3Ti in the new grain refiner. It could offer a two-stage reduction of misfit during nucleation of $\alpha-Al$ in the cast Al-Si alloy. Because the $MgAl_2O_4$ is a rather stable compound, the participate of $MgAl_2O_4$ could make AlTiB grain refiner to be more stable.

Figure 7 depicts the average grain sizes of A356 alloys treated by inoculation with different grain refiners. It is clear that the grain size became coarse with the prolonged holding after inoculation with all the three grain refiners. However, both $Al_{1.5}Ti_1B$ and $Al_{2.5}Ti_{2.5}B$ provide worse coarsening than $Al_{2.2}Ti_1B-S$. Although the reduction of the grain size could be obtained by $Al_{1.5}Ti_1B$ and $Al_{2.5}Ti_{2.5}B$ within a short period of time after inoculation, the $Al_{2.5}Ti_{2.5}B$ were all the further reduction in grain size was achieved after adding $Al_{2.2}Ti_1B-S$. With the increase in holding time, there is an obvious loss of refinement potency in Al by $Al-5Ti-1B$. The average grain size with the holding time of 60 min is 1083 nm which is about

twice that achieved with 5 min. Applying RMF to the inoculated Al, the average grain size can be further reduced with magnetic flux densities of 6 and 12 mT and shows a small fluctuation with the prolongation of holding time. However, when the magnetic flux density of RMF increases to 18 mT, the mean grain size is coarser than that obtained using single inoculation. the

Figure 5 shows the tensile properties of A356 alloys treated with different grain refiners. As expected, the refined microstructure could improve the tensile properties of A356 alloys. After T6 heat treatment, the elongation of A356 alloys was 3.8%, 6.8% and 7.8%, respectively, when treated without grain refiner, Al5i1B and Al2.2Ti1B-S. It was interesting that the refinement using Al2.2Ti1B-S could double the elongation of A356 alloy than that without refinement. The yield strength was 232.7MPa, 242.8MPa and 256.6MPa, respectively, for the A356 alloys treated without grain refiner, Al5i1B and Al2.2Ti1B-S. Similarly, the ultimate tensile strength (UTS) was 280.0MPa, 304.7MPa, 313.0MPa, respectively, for the A356 alloys treated without grain refiner, Al5i1B and Al2.2Ti1B-S. Compared to the tensile properties of A356 alloy without refinement, the yield strength and UTS were increased 10.1MPa and 24.7MPa after refining by Al5Ti1B, and 23.9MPa and 33.0MPa after refining by Al2.2Ti1B-S.

The improvement of mechanical properties through grain refinement can be explained by Hall-Petch mechanism. The yield strength and elongation of materials are proportional to the grain sizes. The smaller the grain size, the better the yield strength can be achieved. In addition, the grain refinement also significantly affects the size and morphology of eutectic Si. As seen in Fig.6, T6 heat treatment could change the morphology of eutectic Si phase from fibrous to spheroidal. This could reduce the concentration of stress and prevent the formation of microcracking under load. Therefore, the elongation and tensile strength could be improved. The detailed size

distribution of Si phase is shown in figure 6 d, e and f for the A356 alloy treated at different conditions. The average size of Si phase was 2.26 μm , 2.18 μm and 2.34 μm in the A356 without refinement, refined by Al5Ti1B and Al2.2Ti1B-S respectively. Clearly, the average sizes were very close in the experimental three alloys. However, the size distribution was quite different. The size distribution in the A356 without refinement showed a single peak at 1.5-3 μm . After refined by Al5Ti1B, it was still a single peak at 1.0-2.3 μm . However, when using Al2.2Ti1B-S grain refiner, the distribution of Si phase was a double peak. The first peak was at 0.7-1.4 μm and the second one was at 1.6-2.6 μm . Therefore, the double peak distribution of Si phase would be beneficial to the enhancement of tensile strength and elongation of A356 alloy.

5. Conclusions

The grain refinement in A356 alloy has been enhanced by introducing extra Mg and increasing the reaction time to form MgAl_2O_4 in the master alloy. The synthesized Al2.2Ti1B-S refiner is more effective than Al5Ti1B refiner because the grain size is ** after refining by Al2.2Ti1B-S and is ** after refinement by Al5Ti1B. The tensile property of the A356 alloy is improved by using Al2.2Ti1B-S compared to the properties of A356 alloy refined by Al5Ti1B. The ultimate tensile strength, yield strength and elongation are increased by 8.3MPa, 13.8MPa and **, respectively, for the A356 alloy refined by Al5Ti1B and Al2.2Ti1B-S. The significant improvement of mechanical properties is attributed to the effective nucleation of $\alpha\text{-Al}$ and the double-peak size distribution of eutectic Si phase. The formation of MgAl_2O_4 layer on the TiB_2 surface might play the vital role for the improvement of grain refinement.

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References

- [1] Y. Zhang, N. Ma, Y. Le, S. Li, H. Wang, Mechanical properties and damping capacity after grain refinement in A356 alloy, *Mater. Lett.* 59 (2005) 2174–2177.
- [2] D.G. McCartney, Grain refining of aluminium and its alloys using inoculants, *Int. Mater. Rev.* 34 (1989) 247–260.
- [3] B.S. Murty, S.A. Kori, M. Chakraborty, 2002----IMR----Grain refinement of aluminium and its alloys by heterogeneous nucleation and alloying.pdf, *Int. Mater.* 47 (2002) 3–29.
- [4] A.. Bunn, P. Schumacher, M.A. Kearns, C.B. Boothroyd, A.L. Greer, Grain refinement by Al–Ti–B alloys in aluminium melts: a study of the mechanisms of poisoning by zirconium, *Mater. Sci. Technol.* 15 (1999) 1115–1123. doi:10.1179/026708399101505158.
- [5] S. a Kori, B.S. Murty, M. Chakraborty, Influence of silicon and magnesium on grain refinement in aluminium alloys, *Mater. Sci. Technol.* 15 (1999) 986–992.
- [6] Y.C. Lee, a. K. Dahle, D.H. StJohn, J.E.C. Hutt, The effect of grain refinement and silicon content on grain formation in hypoeutectic Al–Si alloys, *Mater. Sci. Eng. A.* 259 (1999) 43–52. doi:10.1016/S0921-5093(98)00884-3.
- [7] S.A. Kori, B.S. Murty, M. Chakraborty, Development of an efficient grain refiner for Al–7Si alloy, *Mater. Sci. Eng. A.* 280 (2000) 58–61.
- [8] Y. Birol, A novel Al–Ti–B alloy for grain refining Al–Si foundry alloys, *J. Alloys Compd.* 486 (2009) 219–222. doi:10.1016/j.jallcom.2009.07.064.
- [9] T. Wang, H. Fu, Z. Chen, J. Xu, J. Zhu, F. Cao, T. Li, A novel fading-resistant Al–3Ti–3B grain refiner for Al–Si alloys, *J. Alloys Compd.* 511 (2012) 45–49. doi:10.1016/j.jallcom.2011.09.009.
- [10] P.S. Mohanty, J.E. Gruzleski, Grain refinement mechanisms of hypoeutectic Al–Si alloys, *Acta Mater.* 44 (1996) 3749–3760. doi:10.1016/1359-6454(96)00021-3.
- [11] Y. Zhang, N. Ma, H. Wang, Y. Le, S. Li, Effect of Ti and Mg on the damping behavior of in situ aluminum composites, *Mater. Lett.* 59 (2005) 3775–3778.
- [12] Y. Zhang, N. Ma, H. Wang, Y. Le, S. Li, Effect of Ti on the damping behavior of aluminum composite reinforced with in situ TiB₂ particulate, *Scr. Mater.* 53 (2005) 1171–1174.
- [13] H.T. Li, Y. Wang, Z. Fan, Mechanisms of enhanced heterogeneous nucleation during solidification in binary Al–Mg alloys, *Acta Mater.* 60 (2012) 1528–1537. doi:10.1016/j.actamat.2011.11.044.
- [14] T.E. Quested, A.L. Greer, The effect of the size distribution of inoculant particles on as-cast grain size in aluminium alloys, *Acta Mater.* 52 (2004) 3859–3868. doi:10.1016/j.actamat.2004.04.035.
- [15] Z. Fan, Y. Wang, Y. Zhang, T. Qin, X.R. Zhou, G.E. Thompson, T. Pennycook, T. Hashimoto, Grain refining mechanism in the Al/Al–Ti–B system, *Acta Mater.* 84 (2015) 292–304. doi:10.1016/j.actamat.2014.10.055.

¹ Greer A L, Cooper P S, Meredith M W, Schneider W, Schumacher P, Spittle J A, Tronche A, *Advanced Engineering Materials*, 5 (2003) 81-91

² Greer A L, Cooper P S, Meredith M W, Schneider W, Schumacher P, Spittle J A, Tronche A, *Advanced Engineering Materials*, 5 (2003) 81-91.

³ Qian M, Cao P, Easton M A, McDonald S D, StJohn D H, *Acta Materialia*, 58 (2010) 3262-3270.

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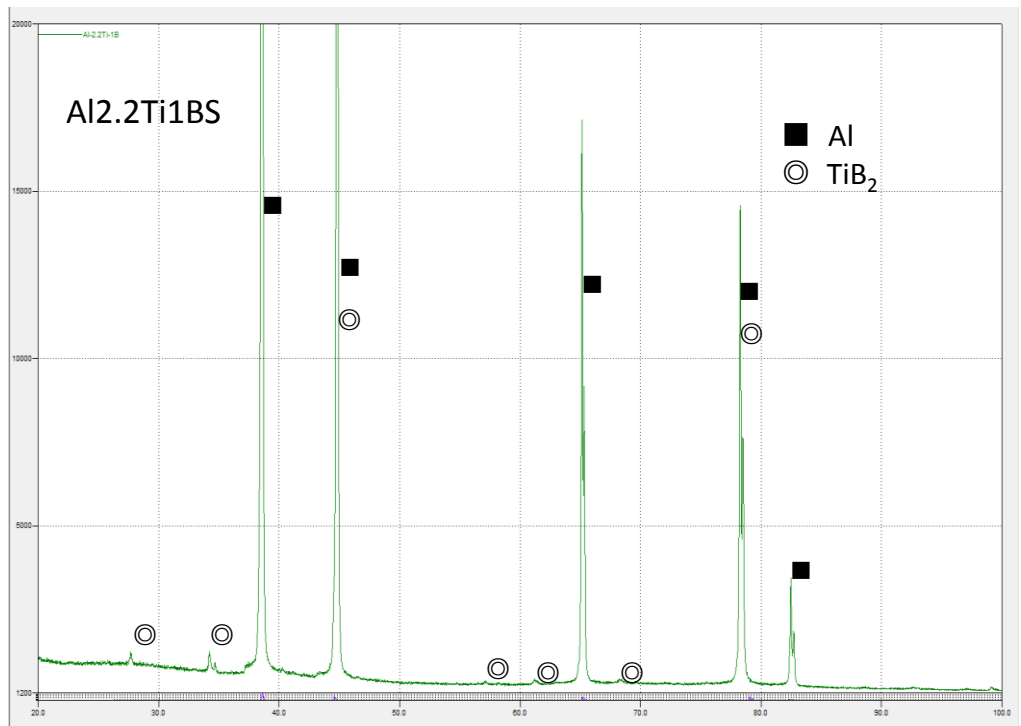


Figure 1 XRD pattern of the Al-2.2Ti-1B-S master alloy for grain refinement.

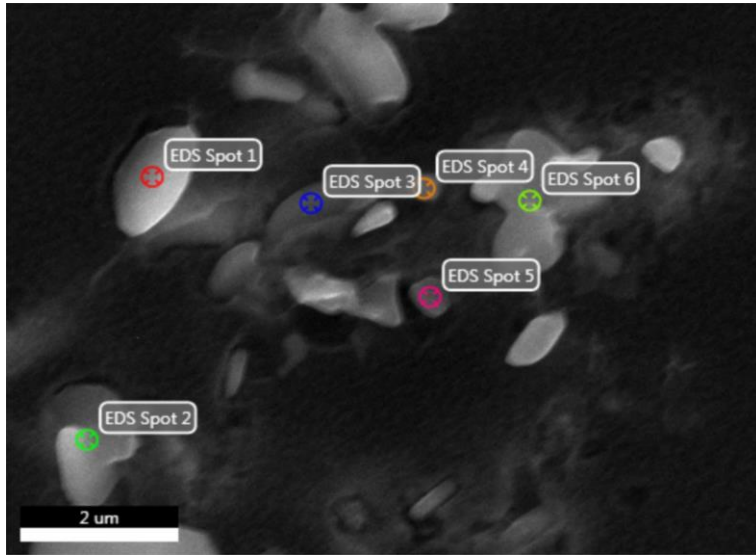


Figure 2 The size and morphology of TiB₂ particles in the Al_{2.2}Ti₁B-S master alloy.

Table Chemical compositions of selected particles

Areas	Chemical composition (wt.%)					
	O	Al	Si	Ti	Fe	Mg
Spot 1	14.06	53.65	0.37	31.54	0.38	/
Spot 2	14.47	49.26	0.46	34.39	0.66	0.76
Spot 3	7.28	62.55	0.48	29.24	0.44	/
Spot 4	9.84	71.17	2.47	13.89	2.67	/
Spot 5	7.59	72.80	0.61	18.03	0.33	0.63
Spot 6	8.98	56.94	2.18	29.00	2.90	/

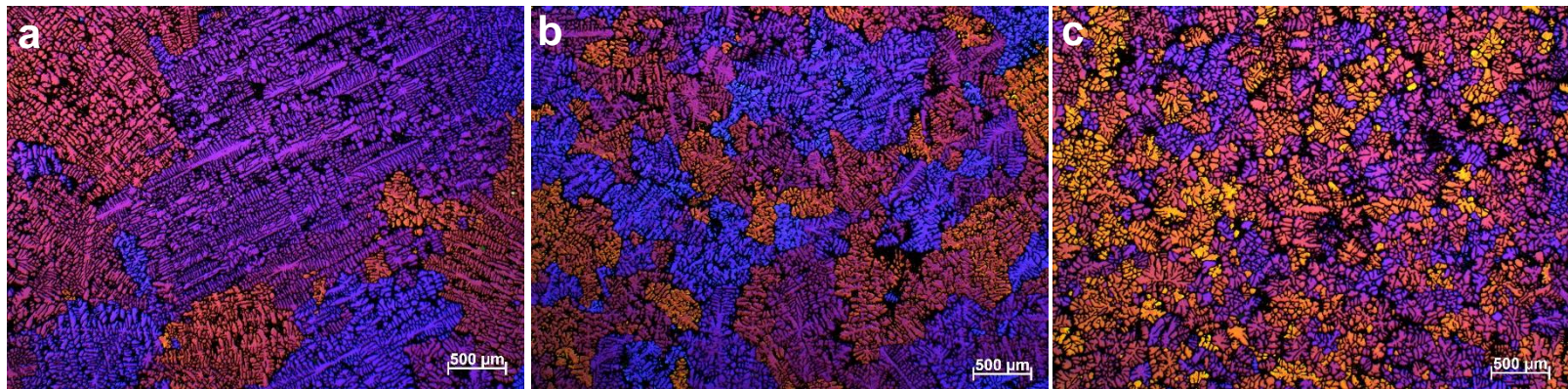


Figure 3 Optical micrographs showing the grain size of A356 alloy treated (a) without grain refinement, (b) with addition of 0.2wt% of Al5Ti1B master alloy and (c) with addition of 0.2wt.% of Al2.2Ti1B-S master alloy.

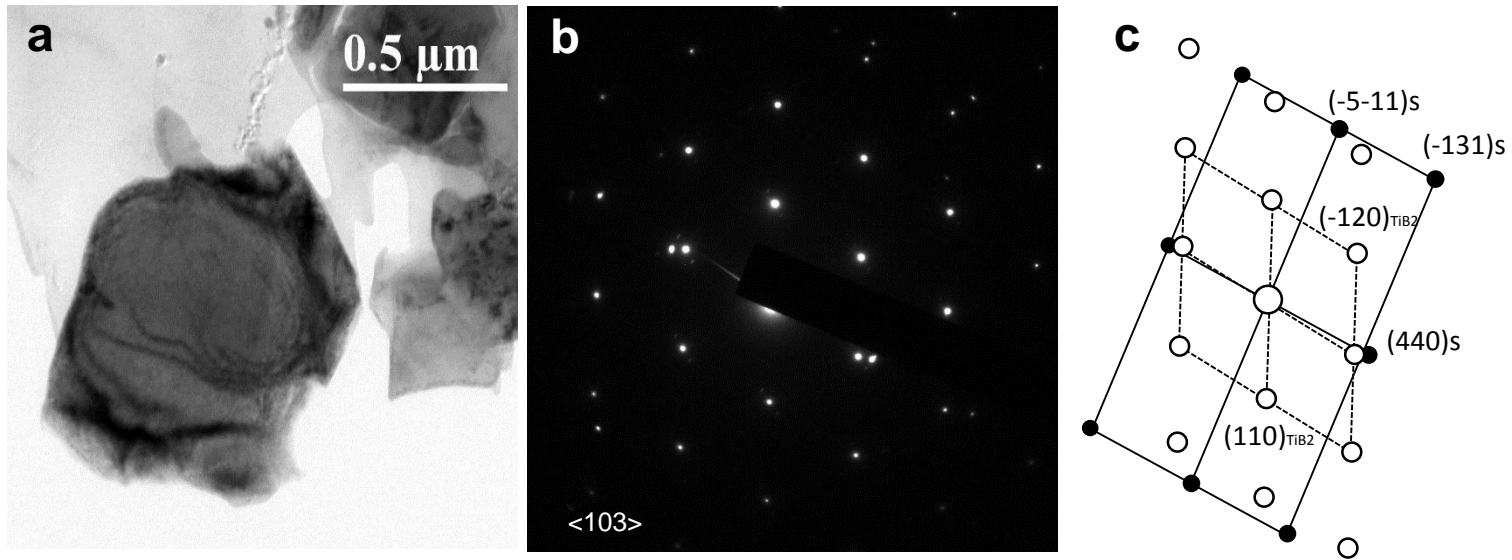


Figure 4 (a) A bright field TEM micrograph showing the TiB₂ particles in the Al_{2.2}Ti₁B-S master alloy, (b) selected area diffraction pattern (SADP) at the particle/Al interface in the Al_{2.2}Ti₁B-S master alloy, and (c) index pattern of TiB₂ and MgAl₂O₄.

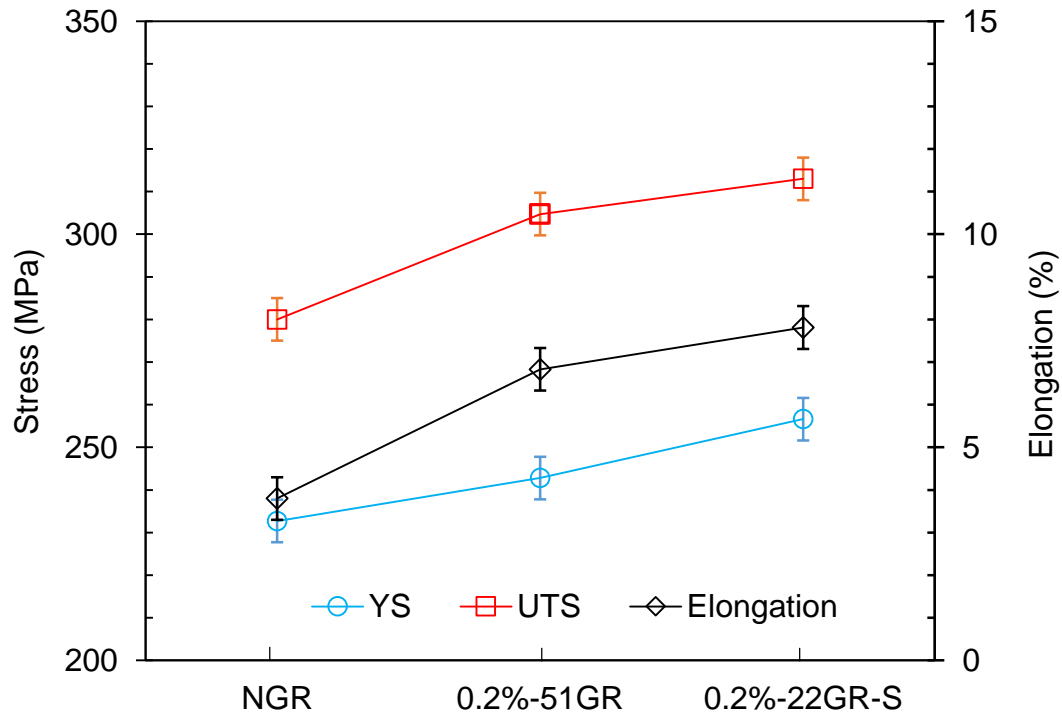


Figure 5 the performance of grain refinement of different refiners on the mechanical properties of A356 alloy

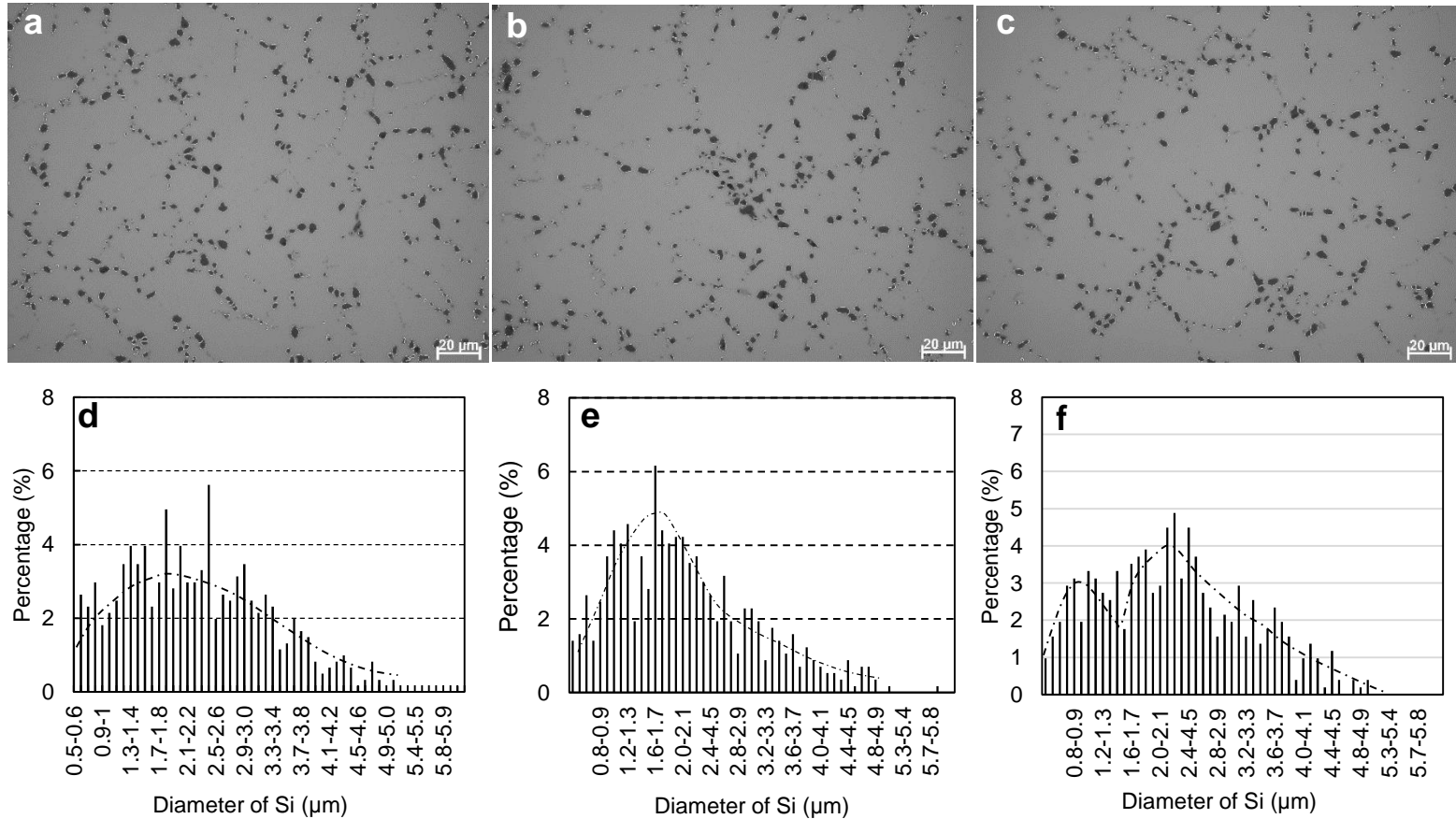


Figure 6 The morphology and distribution of eutectic Si phase in A356 alloy under T6 condition and treated with different grain refiners, (a) without grain refinement, (b) with addition of 0.2wt.% of Al₅Ti₁B master alloy, and (c) with addition of 0.2wt.% of Al_{2.2}Ti₁B-S master alloy.

Table 1 The chemical compositions of A356 alloys treated with different grain refiners.

Materials	Refinement status	Chemical compositions							
		Si	Fe	Cu	Mn	Mg	Sr	Ti	B
	without refinement	6.59	0.078	0.001	0.043	0.289	0.012	0.108	/
A356	Addition of 0.2% Al5Ti1B	6.68	0.076	0.001	0.042	0.279	0.010	0.142	0.002
	Addition of 0.2% Al2.2Ti1B-S	6.74	0.085	0.001	0.045	0.296	0.011	0.112	0.002