

Influence of TiB₂ Particles on Modification of Mg₂Si Eutectic Phase in Al–Zn–Si–Mg–Cu Cast Alloys

Byung Joo Kim, Sung Su Jung, Yong Ho Park, and Young Cheol Lee

Abstract

In this study, the effect of TiB₂ particles on the modification of eutectic phase in Al–Zn–Si–Mg–Cu system alloys is investigated. The microstructure showed that an excellent effect can be achieved after the addition of TiB₂ particles. The morphology of eutectic Mg₂Si changed from large Chinese script to fine polygonal shape with a significant reduction in size. Modified eutectic Mg₂Si particles were investigated using an optical microscope and field emission scanning/transmission electron microscope, and it was confirmed that TiB₂ particles acted as nucleation sites for the eutectic Mg₂Si phase, and the grain size change of Al–Zn–Si–Mg–Cu alloy with increasing TiB₂ contents was analyzed by polarizing microscope. The mechanical properties were also improved by the modified of eutectic Mg₂Si phase. This manuscript also investigated the reason for the improvement in mechanical properties with the modification of the microstructures. Upon these results, a possible mechanism of eutectic Mg₂Si phase modification by the addition of TiB₂ particles is proposed.

Keywords

Aluminum alloys • Phase modification • Intermetallic compound • Mechanical properties

Introduction

The transition of the intermetallic compound morphology in aluminum alloys, also called phase modification, is commonly used in industry to improve mechanical properties, especially ductility. Intermetallic compounds that form during solidification appear in various shapes and sizes, and there are three general morphologies, namely as needles, Chinese script and polyhedral or star-like crystals. Due to the edges or tips of these morphologies serious stress concentration is induced in the matrix, which leads to brittleness of the material. Conversely, the spherical or polygonal type does not concentrate the force and has minimal adverse effect on the elongation of the material. Thus, modification of intermetallic compounds is usually required to improve the mechanical properties of cast components.

Mg₂Si intermetallic compounds are used as core hardened phases in aluminum alloys containing Mg and Si (like as 6XXX) because of their high hardness (4500 MNm⁻²), low density (1.99 × 10³ kgm⁻³), high elastic modulus (120 GPa), high melting temperature (1085 °C), and low coefficient of thermal expansion (7.5 × 10⁻⁶ K⁻¹) [1, 2]. The shape and size of intermetallic compounds have a great influence on the mechanical properties of aluminum alloy [3]. However, in general casting conditions, the final microstructure of Mg₂Si intermetallic compound became coarse with dendritic morphology. This morphology of the Mg₂Si phase is a weakness of the aluminum alloys. To solve this problem, many studies of the Mg₂Si phase modification have been carried out such as P [4, 5], Sr [6], Na [7] and TiB₂ [8, 9] addition. In our previously study, large amount of TiB₂ particles (about 1 wt% Ti contents) were shown to be very effective in modifying the shape of eutectic Mg₂Si intermetallic [8]. However, the effect of TiB₂ particles during solidification on the eutectic Mg₂Si crystal growth, and why a large amount of TiB₂ is needed to modify eutectic Mg₂Si, are unclear. The purpose of this study is to study the relationship of TiB₂ and Mg₂Si phases in Al–8Zn–6Si–4Mg–2Cu cast

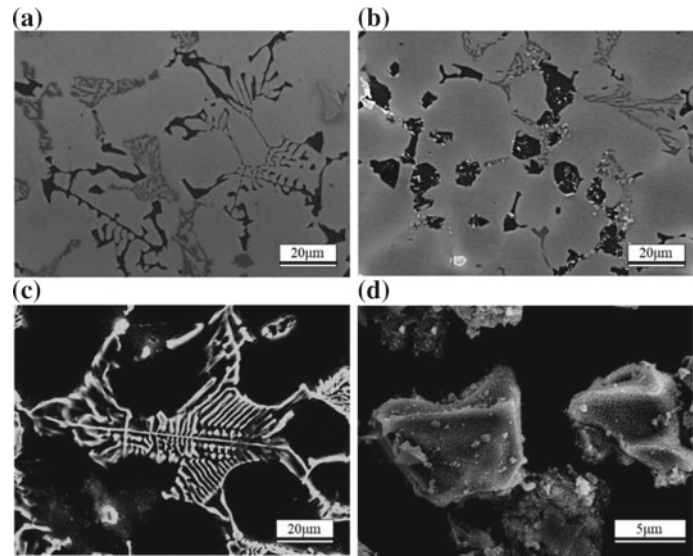
B. J. Kim (✉) · S. S. Jung · Y. C. Lee
Energy Plant Group, Korea Institute of Industrial Technology,
Busan, 46938, Korea
e-mail: kbj@kitech.re.kr

S. S. Jung
e-mail: Jungss@kitech.re.kr

Y. C. Lee
e-mail: yclee87@kitech.re.kr

Y. H. Park
Department of Materials Science and Engineering, Pusan National
University, Busan, 46241, Korea
e-mail: yhpark@pusan.ac.kr

Fig. 1 Microstructure of the eutectic Mg_2Si phase of Al–8Zn–6Si–4Mg–2Cu alloy; **a** and **c** without Al–5Ti–1B master alloy; **b** and **d** with the Al–5Ti–1B master alloy at 1 wt% Ti content



alloys. The mechanism of change in the direction of Mg_2Si crystal growth during the solidification process is also discussed.

Experiments

Al–8Zn–6Si–4Mg–2Cu– x Ti ($x = 0, 0.1, 0.5, 1$ wt%) alloys were produced by gravity-casting. A 20 kHz high frequency furnace was used for melting the alloys. These alloys were prepared by adding pure Zn (99.99%), Mg (99.9%), Cu (99.997) ingot, Si (99.9%) crystalline and Al–5Ti–1B master alloy rods to aluminum molten (99.7%) held at 710 ± 5 °C. After adding the elements, the molten alloys were held for 10 min to assure alloying additions dissolution and melt homogenization. Cast for metallographic specimens were prepared using a cylinder mold (32 Dia. \times 70 mm, FC25 cast iron) preheated to 250 °C. Microstructures were examined using a polarizing microscope, a FE-SEM, FIB and a 200 kV FE-TEM. Deep etching was carried out in 20% NaOH water solution to confirm the 3-dimensional morphology of the eutectic Mg_2Si phase. 2% Fluoboric acid water solution was used as etchant to electrolytic etching, and grain size measurement was according to ASTM E1382. The tensile test were carried out according to the ASTM E8 M using the universal testing machine.

Results

Figure 1a, b show the morphology of the eutectic Mg_2Si phase when Al–5Ti–1B master alloy was added to Al–8Zn–6Si–4Mg–2Cu alloy at 0, 1 wt%. Ti contents. Figure 1c, d

shows the change of morphologies of eutectic Mg_2Si before and after modification by deep etching. In Fig. 1a, c, without Al–5Ti–1B addition, coarse Chinese script type eutectic Mg_2Si phase can be clearly observed. When Ti was added, eutectic Mg_2Si morphology changed to a polygonal shape, less than 10 μm in size (Fig. 1b, d). TiB_2 particles with bright contrast were also observed inside and outside the modified eutectic Mg_2Si in the same figure.

Optical microscope images of microstructure after electrolytic polishing of Al–Zn–6Si–4Mg–2Cu alloy with different Al–5Ti–1B addition amounts are shown in Fig. 3. It can be seen that the grains are clearly determined according to the different color contrast of grains. When 0.1 wt% of Ti was added, the grain size decreased from about 322–120 μm , and there was no further grain refinement, even when the Ti addition amount was increased to 1 wt%.

In the Al–8Zn–6Si–4Mg–2Cu alloy, the eutectic Mg_2Si phase was observed at the inner edge of the aluminum grain (Fig. 2b). As the amount of Ti was increased, more modified eutectic Mg_2Si phases were observed. Interestingly, polygonal shaped Mg_2Si phases were observed in the grain boundaries, as opposed to Chinese script type morphology (Fig. 2h).

Figure 3 shows the change of mechanical properties of aluminum alloy with different contents of Ti wt% [8]. As the content of Ti increases to 1 wt%, the mechanical properties also increase. Yield strength increased from 175–206 MPa and tensile strength increased from 195–253 MPa. The highest increase was the elongation, increasing from 0.63 to 1.05%.

Shapes like Fig. 1a are brittle to mechanical load, because the stress is easily concentrated at the tip. This stress concentration is reduced as the shape of the intermetallic

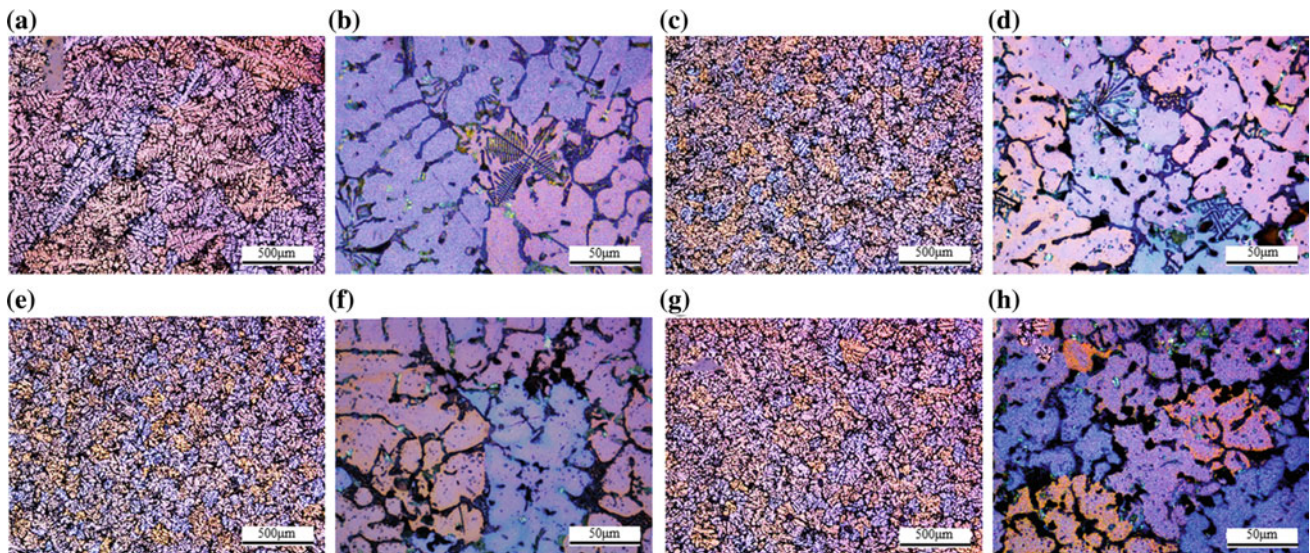
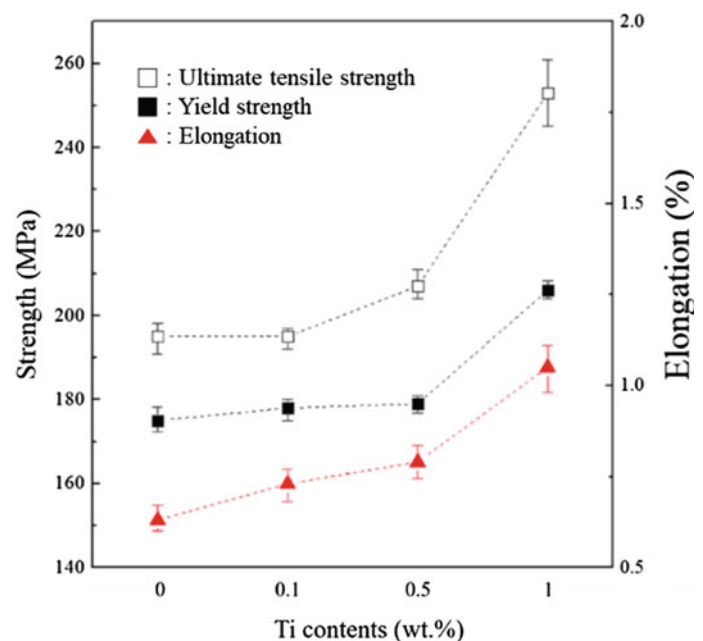


Fig. 2 Optical microscope images of the Al-8Zn-6Si-4Mg-2Cu alloys after electrolytic polishing: **a, b** no Ti, **c, d** 0.1 wt% Ti, **e, f** 0.5 wt% Ti, **g, h** 1 wt% Ti

Fig. 3 Mechanical properties of Al-8Zn-6Si-4Mg-2Cu alloys with different Ti contents [8]



compound becomes smaller and rounder. As the added TiB₂ particles, the eutectic phase of Chinese script shape changes to polygonal shape. As the Ti content was added by 1 wt%, Most of the eutectic phases were modified, which greatly increased the mechanical properties.

Figure 4 shows a cross-section of the modified eutectic Mg₂Si phase measured by TEM/EDS. Al, Mg, Si, Ti and B elements were detected by EDS. It confirms that a phase containing Ti, B is observed inside of the modified Mg₂Si. Analysis of the crystal orientation of Mg₂Si and TiB₂ by HR-TEM is shown.

Discussion

As shown in Fig. 1, the eutectic Mg₂Si phase was modified by the addition of Al-5Ti-1B master alloys. In previous studies, it was reported that TiB₂ particles in the Al-5Ti-1B master alloy modified the eutectic Mg₂Si phase [8]. Figure 2b, d show that the eutectic Mg₂Si phase was observed at the inner edge of the aluminum grains. Figure 5 shows the solidification mechanism of the eutectic Mg₂Si phase in the Al-8Zn-6Si-4Mg-2Cu alloy. Figure 5a shows the

Fig. 4 TEM/EDS analysis data of modified eutectic Mg_2Si phase

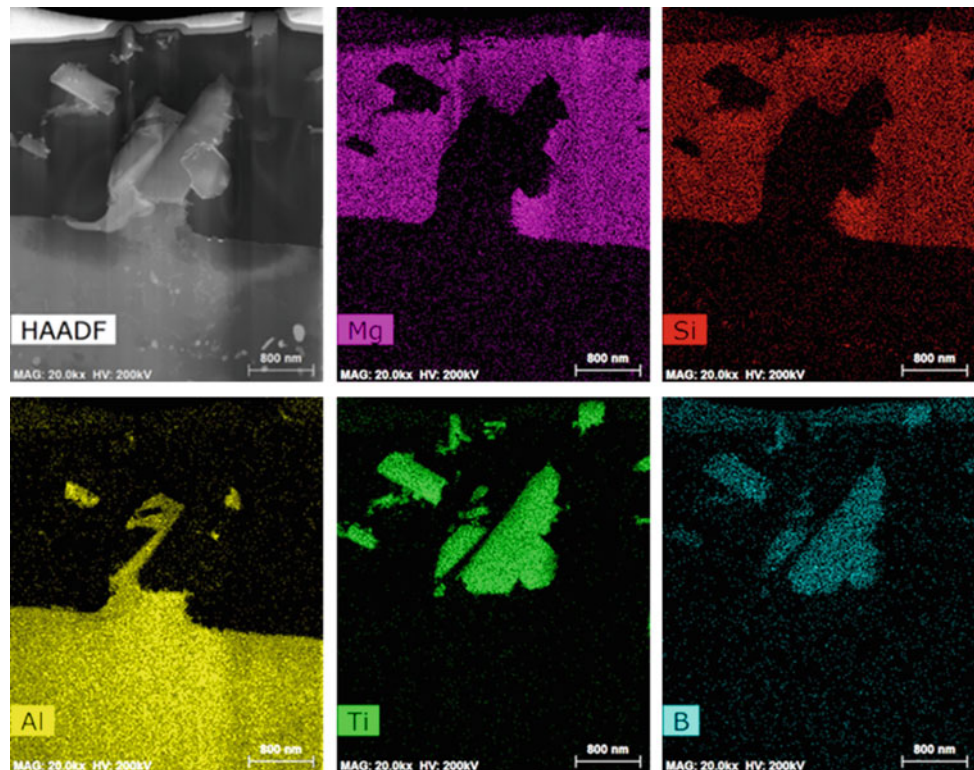
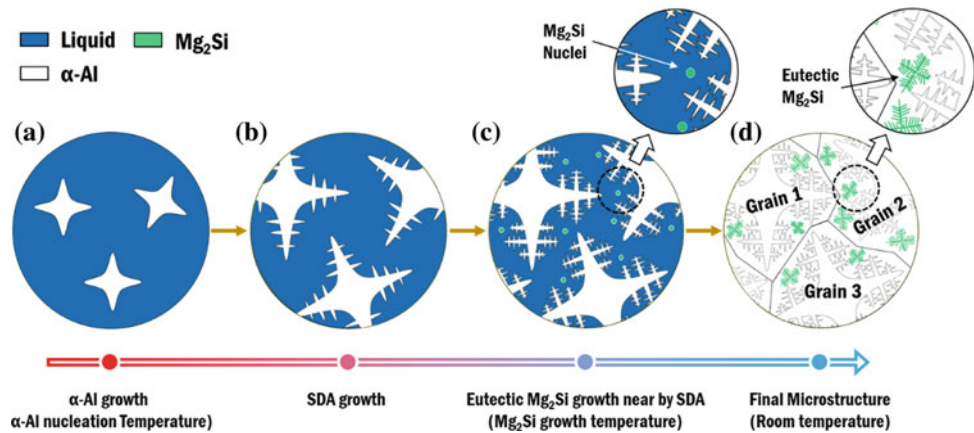


Fig. 5 Schematic illustrations presenting the stages in microstructural evolution during solidification of eutectic Mg_2Si with no TiB_2 particles

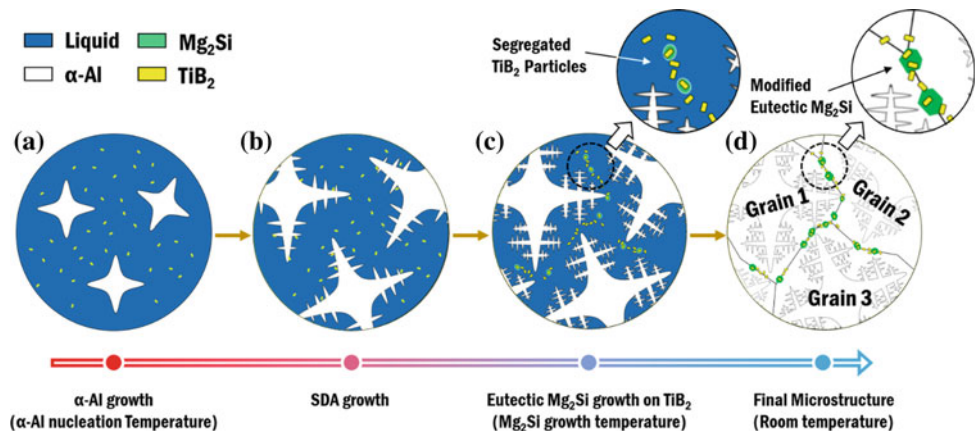


nucleation and growth of primary aluminum dendrite. Figure 5b shows the growth of secondary dendrite arms (SDA) due to growth and coarsening of aluminum dendrites. Segregation of the solute element (Mg, Si) occurs during the growth of aluminum grains. In SDA where Mg and Si elements are segregated, the Mg_2Si nuclei form due to the compositional supercooling. Therefore, nuclei of eutectic Mg_2Si generate around the SDA and grow into Chinese script morphology (Fig. 5d). While the eutectic Mg_2Si phase grows near the SDA, the $\alpha-Al$ also grows and these two phases come into contact during solidification. Segregation of solvent elements (Al) occurs around the growing eutectic Mg_2Si phase, the edge of Chinese script morphology has a

low potential for the contacted $\alpha-Al$. For this reason, $\alpha-Al$ will easily engulf the eutectic Mg_2Si , and as a result, the eutectic Mg_2Si phase solidifies at the edge of the grain as shown in Figs. 2b, d, and 5d.

The solidification path of the Al-8Zn-6Si-4Mg-2Cu alloy has been reported to proceed in the order of $\alpha-Al \rightarrow Mg_2Si \rightarrow Si \rightarrow Al_5Cu_8Si_6Mg_2$ [8]. The particle pushing of TiB_2 particles by $\alpha-Al$ is known in many research [10, 11]. Particularly, the agglomerated TiB_2 particles have a high potential at the interface with the growing aluminum, and they are easily pushed by the growing aluminum [11]. TiB_2 particles also act as good nucleation sites on Mg_2Si because the crystal arrangement at the interface between the

Fig. 6 Schematic illustrations presenting the stages in microstructural evolution during solidification of eutectic Mg₂Si with TiB₂ particles



(001) of TiB₂ and the (200) of Mg₂Si is similar [9]. In previously studies, and in Figs. 1 and 2 of this work, the modified eutectic Mg₂Si located at grain boundaries and the TiB₂ particles present in and around it suggest the following mechanism: TiB₂ particles were pushed into grain boundaries during the growth of the α -Al grain, and the TiB₂ particles agglomerated in the grain boundaries acted as nucleation sites for eutectic Mg₂Si. Figure 6 shows the solidification mechanism of the eutectic Mg₂Si phase of the Al-8Zn-6Si-4Mg-2Cu alloy with enough TiB₂ particles added. Figure 6a shows the nucleation and growth of primary aluminum as shown in Fig. 5a. As solidification progresses, the agglomerated TiB₂ particles are easily pushed out while the aluminum SDA is growing, because they have a high potential for aluminum (Fig. 6b). At the temperature where the magnesium phase forms, the eutectic Mg₂Si phase nucleate easily from the TiB₂ particles as shown in Fig. 6c. It means that the eutectic Mg₂Si phase nucleates on the TiB₂ substrates and grows in polygonal shape. During the growth of the eutectic Mg₂Si phase with TiB₂ particles, aluminum also grows and these two phases come into contact. Unlike the Chinese script eutectic Mg₂Si, the polygonal eutectic Mg₂Si and the agglomerated TiB₂ particles have a high potential for α -Al and are easily pushed into the grain boundaries. As shown in Figs. 2f, g and 6d, modified Mg₂Si and TiB₂ particles are located in the aluminum grain boundaries.

Another discussion point is the effect of grain refinement with TiB₂ addition on the morphology of eutectic Mg₂Si phase. Al-5Ti-1B master alloy is known as a good grain refiner for aluminum alloys. In this work, Al-5Ti-1B master alloy of 0.1, 0.5, 1 wt% Ti contents were added. With 0.1 wt % Ti addition, the grain size was greatly decreased from 322 to 122 μ m. However, further refinement was not observed with addition of 0.5, 1 wt% Ti contents. As shown in Fig. 2b, d, the morphology and position of eutectic Mg₂Si did not change due to the grain refinement. From these

results, it can be concluded that grain refinement does not affect the solidification mechanism of eutectic Mg₂Si.

Conclusion

1. The eutectic Mg₂Si phase of Al-8Zn-6Si-4Mg-2Cu alloy was modified by adding 1 wt% content of Al-5Ti-1B alloy. TiB₂ particles were observed inside the modified eutectic Mg₂Si phase. The good match of crystal growing orientation between TiB₂ and Mg₂Si was confirmed by TEM analysis. It was confirmed that TiB₂ particles cause modification of eutectic Mg₂Si.
2. The Chinese script type eutectic Mg₂Si was observed at the inner edge of the α -Al grains. Mg₂Si phase of polygonal shape, modified by addition of TiB₂, was observed at grain boundaries. It is believed that heterogeneous nucleation of eutectic Mg₂Si phase take place on the TiB₂ particles and they are pushed into grain boundaries during the growing process. When 1 wt% Ti content of Al-5Ti-1B was added to Al-8Zn-6Si-4Mg-2Cu alloy, there were enough TiB₂ particles to modify most of the eutectic Mg₂Si phase.

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References

1. Lu L, Lai MO, Hoe ML(1998) Formation of nanocrystalline Mg₂Si and Mg₂Si dispersion strengthened Mg-Al alloy by mechanical alloying. *Nanostructured Mater.* 10:551-563.
2. Wang L, Qin XY(2003) The effect of mechanical milling on the formation of nanocrystalline Mg₂Si through solid-state reaction. *Scr. Mater.* 49:243-248.
3. Seifeddine S, Johansson S, Svensson IL (2008) The Influence of cooling rate and manganese content on the β -Al₁₅FeSi phase

- formation and mechanical properties of Al-Si-based alloys. *Mater. Sci. Eng. A* 490:385–390.
4. Tebib M, Samuel AM, Ajersch F, Chen XG (2014) Effect of P and Sr additions on the microstructure of hypereutectic Al-15Si-14Mg-4Cu alloy. *Mater. Charact.* 89:112–123.
 5. Qin QD, Zhao YG, Zhou W, Cong PJ, (2007) Effect of phosphorus on microstructure and growth manner of primary Mg₂Si crystal in Mg₂Si/Al composite. *Mater. Sci. Eng. A* 447:186–191.
 6. Jiang W, Xu X, Zhao Y, Wang Z, Wu C, Pan D, Meng Z (2018) Effect of the addition of Sr modifier in different conditions on microstructure and mechanical properties of T6 treated Al-Mg₂Si in-situ composite. *Mater. Sci. Eng. A* 721:263–273.
 7. Zhang J, Fan Z, Wang Y, Zhou B (2000) Microstructural development of Al-15 wt%Mg₂Si in situ composite with mischmetal addition. *Mater. Sci. Eng. A* 281:104–112.
 8. Kim BJ, Jung SS, Hwang JH, Park YH, Lee YC (2019) Effect of Eutectic Mg₂Si Phase Modification on the Mechanical Properties of Al-8Zn-6Si-4Mg-2Cu Cast Alloy. *Metals (Basel)* 9(1):32.
 9. Li C, Liu X, Zhang G (2008) Heterogeneous nucleating role of TiB₂ or AlP/TiB₂ coupled compounds on primary Mg₂Si in Al-Mg-Si alloys. *Mater. Sci. Eng. A* 497:432–437.
 10. Schaffer PL, Arnberg L, Dahle AK (2006) Segregation of particles and its influence on the morphology of the eutectic silicon phase in Al-7 wt% Si alloys. *Scr. Mater.* 54:677–682.
 11. Han Y, Li K, Wang J, Shu D, Sun B (2005) Influence of high-intensity ultrasound on grain refining performance of Al-5Ti-1B master alloy on aluminium. *Mater. Sci. Eng. A* 405:306–312.