Microstructural Improvement of Eutectic Al + Mg$_2$Si Phases on Al–Zn–Si–Mg Cast Alloy with TiB$_2$ Particles Additions

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Abstract: In this study, the effects of adding TiB$_2$ particles to eutectic Al + Mg$_2$Si phases in aluminum alloys were analyzed. The eutectic Al + Mg$_2$Si phases were modified effectively when a large amount of TiB$_2$ was added, and changes in the shape, size, and distribution of the eutectic Al + Mg$_2$Si phases were confirmed using a polarizing microscope and FE-SEM. The crystal structure of the TiB$_2$ particles and Mg$_2$Si phases were analyzed using HR-TEM, and the analysis confirmed that the TiB$_2$ particles can act as heterogeneous nucleation sites. This paper intends to clarify the principle of phase modification of the eutectic Al + Mg$_2$Si phases by TiB$_2$ particles and proposes a new mechanism to improve Mg$_2$Si phase modification when TiB$_2$ particles are added.

Keywords: aluminum alloy; phase modification; intermetallic compound; eutectic Al + Mg$_2$Si phases

1. Introduction

Mg$_2$Si is an intermetallic compound (intermetallics) with excellent hardness (4.5 × 10^9 N/m$^2$), modulus of elasticity (120 GPa), and low density (1.99 g/cm$^3$) [1,2]. The shape, size, and distribution of Mg$_2$Si phases have a significant effect on its mechanical properties. In Al–Si–Mg alloy systems, Mg$_2$Si phases are crystallized according to the ratio of Si and Mg composition. In as-cast conditions, Mg$_2$Si phases grow in a coarse dendritic shape [3–6]. Coarse dendritic Mg$_2$Si phases lead to nonhomogeneous stress concentration and reduce the mechanical properties of Al alloys. Therefore, improving the morphologies of the Mg$_2$Si phases is a decisive test for Al–Mg$_2$Si alloys. In previous studies, it has been reported that Mg$_2$Si phases in Al-based alloys are improved by the application of microstructure treatment processes such as hot extrusion [7] and modification heat treatment [8]. In addition, Mg$_2$Si phase improvement can be achieved with the addition of P [5,9], Na [10], TiB$_2$ [9,11,12], and Ca/Sb [13,14]. However, most of these studies have focused on the improvement of the primary Mg$_2$Si phase. There are only a few studies that have been conducted on eutectic Al + Mg$_2$Si phases. The shape of the eutectic Al + Mg$_2$Si phases has a great influence on the mechanical properties as well as on the primary Mg$_2$Si phase. In general, only a few hundred ppm additions of alloying elements or agents are expected to yield enough effects for the modification or phase improvement of aluminum alloys [15–17]. However, in the case of Mg$_2$Si some studies have reported that a relatively large amount of TiB$_2$ particles (approximately 5 wt.% [12] and 5 vol.% [18]) were required to effectively improve the eutectic Al + Mg$_2$Si phases of Al–Mg$_2$Si alloys. In our previous work, TiB$_2$ particles (approximately 1 wt.% Ti) effectively improved the eutectic Al + Mg$_2$Si phases of Al-based alloys [11]. There are various types of eutectic (Al + Mg$_2$Si) colonies. Variations in these colonies depend on the contents of Si and Mg such as lamellar, flake-like, rod-like, and irregular...
lamella [19]. In studies of the improvement of eutectic Al + Mg2Si phases, the modified eutectic Al + Mg2Si phases were still eutectic colony types [10,20,21]. Interestingly, the eutectic (Al + Mg2Si) colony was changed to a divorced eutectic colony by the addition of Al–5Ti–1B master alloys. However, there is still insufficient evidence to provide an explanation of the relationship between the relatively large amount of TiB2 particles and the eutectic (Al + Mg2Si) colony improvements. The purpose of this study is to investigate the relationship between TiB2 and eutectic Al + Mg2Si phases in an Al–Zn–Si–Mg–Cu cast alloy. In addition, the modified mechanism of the eutectic Al + Mg2Si phases with TiB2 particles was also confirmed.

2. Materials and Methods

The Al–8Zn–6Si–4Mg–2Cu–xTi (x = 0, 0.1, 0.5, and 1) casting alloy was manufactured using gravity casting. A high-frequency induction melting furnace was used for melting at 680 °C ± 5 °C. The alloy composition (all compositions quoted in this work are given in wt.%) was aligned using commercial Al (99.97%), Zn (99.9%), Mg (99.8%), and Cu (99.9%) ingots; pure crystalline Si (99.9%); and the Al–5Ti–1B master alloy rod. Figure 1 shows the Al–5Ti–1B master alloy as observed through a field emission scanning electron microscope (FE-SEM). As evidenced in Figure 1, the microscope shows the presence of both TiB2 and Al3Ti particles in the Al–5Ti–1B master alloy. The Al–5Ti–1B master alloy was added after all other elements were dissolved entirely. The manufactured alloys were analyzed by optical emission spectrometer (SPECTRO MAXx, SPECTRO, Kleve, Germany), and the composition details of this analysis are shown in Table 1. The specimen for metallographic observation was obtained from the same location as the sample manufactured from the molten metal cylinder mold (32 Ø × 70 mm, FC25 cast iron) preheated to 250 °C. The microstructure was observed using the FE-SEM (S-4800, HITACHI, Tokyo, Japan) polarizing microscope and 200 kV FE-transmission electron microscopy (Talos F200X G2 TEM, Thermo Fisher Scientific, Waltham, MA, USA). A fluoboric acid–distilled water solution was used as an etchant for electrolytic polishing (Lectropol-5, Struers, Copenhagen, Denmark). Average grain size measurements were conducted according to ASTM E1382 standards.

![Figure 1. SEM image of the Al–5Ti–1B master alloy rod: (a) low magnification and (b) high magnification.](image)

| Alloy Components | Zn    | Si    | Mg    | Cu    | Ti    | Al    |
|------------------|-------|-------|-------|-------|-------|-------|
| Al–8Zn–6Si–4Mg–2Cu (Base) | 7.96  | 5.94  | 4.02  | 1.97  | <0.003| bal.  |
| Base + 0.1% of Ti | 7.98  | 5.98  | 4.01  | 1.96  | 0.13  | bal.  |
| Base + 0.5% of Ti | 8.01  | 5.94  | 3.97  | 1.95  | 0.49  | bal.  |
| Base + 1% of Ti   | 7.99  | 6.01  | 4.05  | 2.01  | 1.02  | bal.  |

Table 1. Chemical composition of different Al–5Ti–1B master alloy additions to the Al–8Zn–6Si–4Mg–2Cu–xTi alloys. All values are expressed in weight percent.
3. Results

3.1. Eutectic Al + Mg2Si Phase Modification and Microstructure Change by Al–5Ti–1B Master Alloy Addition

Figure 2 shows the change of the eutectic Al + Mg2Si phases with different Ti amounts in the Al–8Zn–6Si–4Mg–2Cu alloys. The Chinese script-type eutectic Al + Mg2Si phases can be seen in the microstructure of the base alloy. When 0.1% of Ti was added, the shape of the eutectic Al + Mg2Si phases remained a Chinese script type. When 0.5% of Ti was added, both the Chinese script type and polygonal structure of the eutectic Al + Mg2Si phases were observed (Figure 2e). When 1% of Ti was added, the eutectic Al + Mg2Si phases’ morphology changed into a fine polygonal structure (Figure 2b,d). In the same figure, TiB2 particles (indicated by white arrows) can be observed in both the inner and outer parts of the eutectic Al + Mg2Si phases (Figure 2h). Figures 3 and 4 show the polarizing microscope image of the Al–8Zn–6Si–4Mg–2Cu alloy with different amounts of Ti addition. Here, the different colors represent different grains. The average grain size was measured according to ASTM E1382 standards using IMT I-solution DT software (ver. 11.2, IMT i–Solution, Rochester, NY, United States). When 0.1% of Ti was added to the base alloy, the average grain size decreased from 322 to 120 μm. However, no further grain refining was observed when the Ti addition was increased to 1%. While the unmodified eutectic Al + Mg2Si phases were observed at the edges of the Al grains (shown in Figure 4a,b), the modified eutectic Al + Mg2Si phases were observed at the grain boundaries (Figure 4b,c).

![Figure 2](image_url)
Figure 3. Polarized microscope images of the Al–8Zn–6Si–4Mg–2Cu alloy with different amounts of Ti: (a) without Ti; (b) at 0.1% of Ti; (c) at 0.5% of Ti; (d) at 1% of Ti; and (e) the relationship between average grain size and Ti content.

Figure 4. Polarized microscope images (high magnification) of the Al–8Zn–6Si–4Mg–2Cu alloys with different amounts of Ti: (a) without Ti; (b) at 0.1% of Ti; (c) at 0.5% of Ti; and (d) at 1% of Ti. Here, the white dotted line represents the grain boundaries. The white and yellow arrows represent unmodified and modified eutectic Al + Mg2Si phases, respectively.

3.2. TEM/EDS and HR-TEM Results of Modified Eutectic Al + Mg2Si Phases

Figure 5 shows a cross section of the modified eutectic Al + Mg2Si phases analyses by TEM/EDS (Transmission Electron Microscope/Energy Dispersive X-ray Spectroscopy). The Al, Mg, Si, Ti, and B elements were detected. The TiB2 particles (the area where Ti and B signals overlap) are observed inside the modified eutectic Al + Mg2Si phases. Figure 6 shows the TEM micrographs of the modified eutectic Al + Mg2Si phases in the Al–8Zn–6Si–4Mg–2Cu–1Ti alloys. Figure 6a shows the bright field TEM image of the modified eutectic Al + Mg2Si phases. Figure 6b is a high-resolution TEM image of the yellow box in Figure 6a, which shows the interface between Mg2Si and TiB2.
Figure 5. TEM and EDS analysis data of modified eutectic Al + Mg$_2$Si phases in the Al–8Zn–6Si–4Mg–2Cu–1Ti alloy.

4. Discussion

4.1. Nucleation Sites of the Eutectic Al + Mg$_2$Si Phases on the TiB$_2$ Particles

Figure 4 shows that, as the Ti amount increased from 0% to 1%, more of the eutectic Al + Mg$_2$Si phases was modified. The Al–5Ti–1B master alloy usually contains a 1.94 volume fraction of TiB$_2$ particles. Although this volume fraction is low, the Al–5Ti–1B master alloy contains a large amount of TiB$_2$ particles (Figure 1) because TiB$_2$ particles can be as small as 1–4 μm (in Figure 1b). The Al–8Zn–6Si–4Mg–2Cu–1Ti alloy contains a 0.39 volume fraction of TiB$_2$ particles. TiB$_2$ particles were also observed around the modified eutectic Al + Mg$_2$Si phases (Figure 2h). These results indicate that the TiB$_2$ particles acted as nucleation sites for the eutectic Al + Mg$_2$Si phases. However, the eutectic Al + Mg$_2$Si phases were unmodified by the addition of 0.1% (0.04 vol.% of TiB$_2$ particles) and 0.5% of Ti (0.19 vol.% of TiB$_2$ particles). In these Al–8Zn–6Si–4Mg–xTi (x = 0.1 and 0.5) alloys, the amount of TiB$_2$ particles was insufficient to change the shape of the eutectic Al + Mg$_2$Si phases.
phases. When 1% of Ti was added, there was a sufficient number of TiB$_2$ particles to act as nucleation sites for the eutectic Al + Mg$_2$Si phases. For this reason, most of the eutectic Al + Mg$_2$Si phases were modified.

Figure 5 shows the TEM/EDS data for the modified eutectic Al + Mg$_2$Si phases and the TiB$_2$ particles. The TiB$_2$ particles were observed inside the improved eutectic Al + Mg$_2$Si phases and were also contained in the Al–5Ti–1B master alloy used for the Al–8Zn–6Si–4Mg–2Cu–xTi alloys (in Figure 1). Since the melting temperature of TiB$_2$ particles is 3225 °C [22], they did not melt easily at the temperature required to melt the Al alloy. The TiB$_2$ particles could therefore act as heterogeneous nucleation sites for eutectic Al + Mg$_2$Si phases during the solidification process.

Figure 6a shows the TEM images of the modified eutectic Al + Mg$_2$Si phases. TiB$_2$ particles were observed in the modified eutectic Al + Mg$_2$Si phases. Figure 6b is a high-resolution TEM image of the yellow box in Figure 6a. The crystallographic structure of the TiB$_2$ particle and the eutectic Al + Mg$_2$Si phases are clearly observed. The upper section shows the eutectic Al + Mg$_2$Si phases, and the lower section shows the TiB$_2$ particle. The crystal orientations of both phases were measured by HR-TEM. The lattice plane spacing of the lower section crystal (α) is 0.32 nm, which is in agreement with the (0001) plane of the TiB$_2$ crystal structure [3]. The lattice plane spacing of the upper section crystal is 0.323 nm, which is in agreement with the (200) plane of the Mg$_2$Si crystal structure [9]. The stacking order of the (200)Mg$_2$Si plane and the (0001)TiB$_2$ plane is illustrated in Figure 6c. The stacking order of the (200)Mg$_2$Si plane is ABC . . . , where the stacking pattern of Si atoms (ACA . . . ) is observed in Figure 6b. The stacking order of (0001)TiB$_2$ plane is ABA . . . , where the stacking pattern of Ti atoms (AA . . . ) is observed. The atomic patterns of Mg and B are not observed due to differences in zone axis. The dotted line in Figure 6b shows an interface of Mg$_2$Si and TiB$_2$ that is clearly well bonded. The crystal plane of (200)Mg$_2$Si and (0001)TiB$_2$ possesses a low misfit (approximately 4.64%), as calculated by the Turnbull–Vonnegut equation [9]. Therefore, the TiB$_2$ particle clearly acted as the heterogeneous nucleation site for the eutectic Al + Mg$_2$Si phases.

4.2. Eutectic Al + Mg$_2$Si Phase Modification and Microstructure Change by TiB$_2$ Particle Additions

As shown in Figure 2a,b, the morphology of the eutectic Al + Mg$_2$Si phases is in the form of the Chinese script shape. Observations under a polarizing microscope showed the unmodified eutectic Al + Mg$_2$Si phases at the inner edges of the Al grains (in Figure 4a,b). Since the eutectic Al + Mg$_2$Si phases are located inside of the Al grains, it can be concluded that there was eutectic (Al + Mg$_2$Si) growth from the primary Al grains during the solidification process. Figure 7a–d illustrates the microstructural evolution during solidification of the unmodified eutectic Al + Mg$_2$Si phases. Figure 7a demonstrates the formation of the nucleated α-Al by the Al solidification reaction inside the molten metal. Figure 7b shows an interface of Mg$_2$Si and TiB$_2$ that is clearly well bonded. The crystal plane of (200)Mg$_2$Si and (0001)TiB$_2$ possesses a low misfit (approximately 4.64%), as calculated by the Turnbull–Vonnegut equation [9]. Therefore, the TiB$_2$ particle clearly acted as the heterogeneous nucleation site for the eutectic Al + Mg$_2$Si phases.
In the hypoeutectic composition of Al–Mg₂Si alloys, the eutectic Al + Mg₂Si phases solidify after the α-Al phase growth. When the eutectic reaction begins, the eutectic Al + Mg₂Si phases are crystallized in the remaining liquid phase. Therefore, effective improvement of the eutectic Al + Mg₂Si phases occurs only when the TiB₂ particles remain in the liquid phase. However, since the TiB₂ particles have an excellent crystallographic match with the Al phase, most of the TiB₂ particles acted as heterogeneous sites for the α-Al phase [23]. Therefore, a small amount of the TiB₂ particles was easily encased in the Al grains. This is why the eutectic Al + Mg₂Si phases were not effectively improved when 0.1% and 0.5% of Ti were added to the Al–8Zn–6Si–4Mg–2Cu alloys. However, once the TiB₂ particles were sufficiently aggregated in the molten metal, the agglutinated TiB₂ particles had a high potential for the growing liquid (molten metal)/solid (α-Al) interface. Therefore, during the α-Al phase growth, the agglutinated TiB₂ particles were easily pushed out by the Al grains [24–26]. When the eutectic reaction began, a large amount of the TiB₂ particles existed around the SDA of the Al phase.

Figure 7a, e–g demonstrates the solidification mechanism of the eutectic Al + Mg₂Si phases when sufficient TiB₂ particles were added. Figure 7a, e shows the nucleation and growth of α-Al. Here, the TiB₂ particles aggregated in the liquid phase. These particles were pushed out by the Al grains and now exist around the SDA. When the eutectic reaction began, the TiB₂ particles acted as heterogeneous nucleation sites for the eutectic Al + Mg₂Si phases (in Figure 7f). The eutectics Mg₂Si were simultaneously crystallized in the TiB₂ particles’ agglomeration region. The growing eutectic Al + Mg₂Si phases interfered with each other and prevented coarse growth. The TiB₂ particles were located around the grown eutectics Mg₂Si. The α-Al phase also grew during the nucleation of the eutectic Al + Mg₂Si phases. Unlike the unmodified eutectic Al + Mg₂Si phases, the modified eutectic Al + Mg₂Si phases and aggregated TiB₂ particles had a high potential for a liquid/solid interface. They were easily pushed out to the grain boundaries (in Figure 7g). Therefore, in the final microstructure, the modified eutectic Al + Mg₂Si phases and the TiB₂ particles are located at the Al grain boundaries (in Figure 4d).

Another important point of discussion is the effect of grain refinement by the addition of TiB₂ on the shape of the eutectic Al + Mg₂Si phases. The Al–5Ti–1B master alloy is a well-known Al grain refiner [27,28]. The average grain size was greatly reduced from 322 to 122 μm when 0.1% Ti was added to the Al–8Zn–6Si–4Mg–2Cu alloy. However, when either 0.5 or 1 wt.% Ti was added, the grains were not further refined. As seen in Figure 4a,b, the shape and location of eutectic Al + Mg₂Si phases did not change due to grain refinement.
Therefore, grain refinement does not affect the modification of the eutectic Al + Mg$_2$Si phases.

4.3. Effect of the Addition of TiB$_2$ Particles to Al–8Zn–6Si–4Mg–2Cu Alloys

The effect of the addition of TiB$_2$ particles on the mechanical properties of the Al–8Zn–6Si–4Mg–2Cu alloys is given in Figure 8 [11]. A tensile test of the Al–8Zn–6Si–4Mg–2Cu–xTi ($x = 0, 0.1, 0.5,$ and 1) alloy was conducted according to ASTM E8 standards. Elongations of individual alloys used strain values at the time of tensile failure. The value of yield strength was confirmed by the “0.2 off-set” method. The morphology of eutectic Al + Mg$_2$Si phases significantly affected its mechanical properties. Yield strength, ultimate tensile strength, and elongation were increased by the addition of TiB$_2$ particles (Figure 8b). While the Ti content increased to 0.5%, the tensile behavior of the Al–8Zn–6.4Si–4Mg–2Cu–xTi ($x = 0, 0.1,$ and 0.5) alloys did not change significantly (Figure 8a). However, when 1% Ti was added, the mechanical properties increased significantly. In the Al–8Zn–6.4Si–4Mg–2Cu–xTi ($x = 0, 0.1, $ and 0.5) alloys, eutectic Al + Mg$_2$Si phases were coarse, irregular, and located at the end of the aluminum grains. The tips of the unmodified Mg$_2$Si were close to the aluminum grains and led to nonhomogeneous stress concentrations. Therefore, the unmodified Mg$_2$Si phase caused micro-cracks and intergranular fracture. This provides an explanation for why the mechanical properties did not increase significantly. However, modified eutectic Al + Mg$_2$Si phases caused homogeneous stress concentration. Since modified eutectic Al + Mg$_2$Si phases were located at the boundary of the aluminum grains, it prevented the propagation of intergranular fracture. Therefore, the mechanical properties of the Al–8Zn–6Si–4Mg–2Cu–1Ti alloy increased significantly.

![Figure 8.](image)

**Figure 8.** (a) Representative strain–stress curve of the Al–8Zn–6Si–4Mg–2Cu–xTi ($x = 0, 0.1, 0.5,$ and 1) alloys; (b) yield strength, elongation, and ultimate tensile strength of the Al–8Zn–6Si–4Mg–2Cu–xTi alloys [11].

5. Conclusions

The eutectic Al + Mg$_2$Si phases of the Al–8Zn–6Si–4Mg–2Cu alloy was effectively modified when 1% of Ti was added. The morphologies of the eutectic structures changed from a coarse Chinese script to a fine polygonal shape. TiB$_2$ particles were observed in the modified eutectics Mg$_2$Si. The crystal structures of both phases were analyzed by HR-TEM to confirm that the TiB$_2$ particles were excellent heterogeneous nucleation particles for Mg$_2$Si.

The modified Mg$_2$Si phase moved from the inside of the grain to the grain boundary, and TiB$_2$ particle clustering around the improved phase was observed. The TiB$_2$ particles agglomerated in the molten Al alloy were easily pushed by the growing primary Al. These particles could remain in the residual molten metal until the eutectic Al + Mg$_2$Si phases’ solidification temperature was reached. However, individual TiB$_2$ particles were easily
surrounded by the growing primary aluminum matrix and did not have a significant effect on the improvement of the eutectic Al + Mg$_2$Si phases.

**Author Contributions:** Writing—original draft, B.K.; writing—review and editing, Y.P. and Y.L.; Supervision, Y.L.; Visualization, B.K.; Conceptualization, J.H. and Y.L.; Investigation, B.K. and J.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This study was conducted with the support of the Korea Institute of Industrial Technology as “Development of root technology for multi-product flexible production (kitech EO–21–0008)”.

**Institutional Review Board Statement:** Not applicable.

**Data Availability Statement:** The raw data required to reproduce these findings are available for download from http://dx.doi.org/10.17632/23zxhtgmht.1 (accessed on 21 October 2020).

**Conflicts of Interest:** The authors declare no conflict of interest.

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