Article

Effect of Eutectic Mg$_2$Si Phase Modification on the Mechanical Properties of Al-8Zn-6Si-4Mg-2Cu Cast Alloy

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Abstract: The modification effect of Al-5Ti-1B master alloy on eutectic Mg$_2$Si in Al-Zn-Si-Mg system alloy was investigated in this study. The microstructure shows that an extreme effect can be achieved after the addition of Al-5Ti-1B master alloy into the base alloy. The morphology of eutectic Mg$_2$Si changed from Chinese script to fine polygonal shape, and the size was refined from over 50 $\mu$m to under 10 $\mu$m. This morphology change is believed to be due to TiB$_2$ particles existing in Al-5Ti-1B master alloy, and the presence of TiB$_2$ particles inside the modified Mg$_2$Si was confirmed by scanning electron microscope/energy dispersive spectrometer (SEM/EDS) observation. The mechanical properties were also improved by the addition of Al-5Ti-1B master alloys. This study investigated the reason for the improvement in mechanical properties with the modification of the microstructure.

Keywords: aluminum alloys; intermetallic compound; phase modification; eutectic Mg$_2$Si; mechanical properties

1. 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 [1]. 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 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.

The intermetallic compound Mg$_2$Si is a key phase of the aluminum alloys containing Mg and Si. It exhibits high hardness (4500 MNm$^{-2}$), low density ($1.99 \times 10^3$ kgm$^{-3}$), high elastic modulus (120 GPa), high melting temperature (1085 °C), and low coefficient of thermal expansion ($7.5 \times 10^{-6}$ K$^{-1}$) [2,3]. The mechanical properties of aluminum alloys containing Mg$_2$Si are largely dependent on the morphology, size and distribution of Mg$_2$Si phases. The Mg$_2$Si intermetallic compound forms into coarse dendritic primary Mg$_2$Si and Chinese script eutectic Mg$_2$Si. These shapes of Mg$_2$Si cause serious problems in the mechanical properties, because these edges of coarse dendritic primary Mg$_2$Si and tips of eutectic Mg$_2$Si become stress concentration points. Therefore, it is necessary to control the
size, morphology and distribution of the Mg$_2$Si phase in order to improve the mechanical properties of these alloys. Many studies have been conducted to modify Mg$_2$Si to this end. In most of the previous studies, the focus was on modification of the primary Mg$_2$Si, which was done by heat treatment [4] or the addition of a nucleant such as Li [4], Na [5,6], Ni [7], P [8,9], Sr [8,10], AlP [11,12] and TiB$_2$ [12]. However, studies on the modification of eutectic Mg$_2$Si have been undertaken through heat treatment [4,10,13] only, which limits the use of these alloys in industry. Therefore, an easy modification method is required for industrial applications.

Jang has reported that TiB$_2$ particles act as heterogeneous nuclei for modification of primary Mg$_2$Si [12]. However, the effect of TiB$_2$ particles on the eutectic Mg$_2$Si has not been investigated yet. In addition, studies on the modification of eutectic Mg$_2$Si have reported only ambiguous results. The purpose of this paper is to study the effect of Al-5Ti-1B master alloys on the size and morphology of eutectic Mg$_2$Si in Al-8Zn-6Si-4Mg-2Cu alloys. The mechanism of improvement in mechanical properties is also discussed.

2. Experimental Procedures

Alloys of composition Al-8Zn-6Si-4Mg-2Cu, with additions of 0, 0.1, 0.5, 1 wt.% Ti were prepared from a commercial purity Al (99.99%, Nantong Tade Electronic Materials Technical co., Ltd., Jiangsu, China), pure Cu (99.997% RND Korea Co., Gwangmyeong, Korea), pure Zn (99.99%, Sichuan Lande Industry Company Ltd., Chengdu, China), pure Mg (99.9%, Luoyang Hualing Magnesium Co., Ltd, Henan, China), commercial crystalline Si (99.9%, Hoshine Silicon Co., Ltd., Pinghu, China) and Al–5Ti–1B master alloy (Ohryoon Ind. Co., Ltd., Busan, Korea). Melting was carried out in a 5 kg capacity SiC crucible, using a 20 kHz high frequency furnace. The melting was carried out at room temperature without additional protective gas. The degassing process of the molten metal was not carried out. The melting temperature was held at 710 ± 5 °C. After the base alloy had melted, Al-5Ti-1B master alloy rod was introduced into the molten metal. The melt was held for about 10 min to dissolve and homogenize the melt. Before the gravity casting, the molten alloy surface was skimmed and stirred. The cylinder mould (32Φ x 70 mm) for metallographic samples and the y-block mould (Figure 1) for tensile test samples were preheated to 250 °C. Materials of y-Block mould is FC25 cast iron. All tensile specimens were taken from the under part of the y-block sample. The actual amounts of Ti added to the base alloy are given in Table 1. 

![Figure 1. The design of the y-block mould (Unit: mm).](image-url)
Therefore, the final microstructure of Al-8Zn-6Si-4Mg-2Cu alloys will have a composition corresponding to the end of the solidification process. Figure 3b shows that the main intermetallic compound existing in the final microstructure is Mg$_2$Si phases.

Thermo-Calc analyses are conducted under equilibrium solidification condition assuming that the cooling rate is slow enough to have full back diffusion in the solid phases. Therefore, the final microstructure of Al-8Zn-6Si-4Mg-2Cu alloys will have a composition corresponding to the end of the solidification process. Figure 3b shows that the main intermetallic compound existing in the final microstructure is Mg$_2$Si phases.

The solidification path of Al-8Zn-6Si-4Mg-2Cu alloy was calculated by Thermo-Calc computer simulation. Metallographic specimens were taken from the same parts of the cylinder mould, mounted in resin and polished using standard practice. Deep etching was performed using 20% NaCl water solution to remove the aluminum matrix and expose the 3-D morphology of the eutectic Mg$_2$Si phase. Microstructures were analyzed by optical microscope (Upright material microscope, Leica DM 2700M RL/TL, Wetzlar, Germany) field emission scanning electron microscopy with energy dispersive spectrometer (FE-SEM/EDS, MIEA III LMH, Tescan, Brno, Czech Republic).

The tensile tests were carried out according to the ASTM E8M sub-size standard (Figure 2) using the Universal tensile testing machine (Universal tester, AG-IC, 300 kN, Shimadzu, Tokyo, Japan). Tensile test was carried out at a strain rate of 0.5 mm/min, at room temperature. The total elongation of specimens was measured using a 25 mm gauge length extensometer. To ensure correct results, five tensile tests were performed on each experiment and averaged after except for the maximum and minimum results.

![Figure 2. ASTM E8M standard specimen architectonic used for tensile test.](image)

### 3. Results and Discussion

Figure 3 shows the changes in the liquid/solid mass fractions during solidification which are calculated by Thermo-Calc software, and the fraction of each phase is summarized in Table 2. From the results, it is estimated that the primary aluminum begins to solidify at 582.8 °C, Mg$_2$Si solidifies from 554.8 °C. Between 554.8 °C and 539.7 °C, the mass fraction of Mg$_2$Si increases along with aluminum. Therefore, this second reaction indicates that the eutectic Mg$_2$Si growth take place in this region. Silicon appears from 554.8 °C and the mass fraction increases along with Mg$_2$Si and Al, which indicates that a ternary eutectic reaction of Al-Si-Mg$_2$Si take place. The final reaction is an Al$_5$Cu$_2$Mg$_8$Si$_6$ phase forms from 506.6 °C. The ternary reaction creates the largest region in forming solid phase Al + Mg$_2$Si + Si (44.6%), whereas the primary Al and the binary reaction (Al + Mg$_2$Si) each contribute 29.7% and 21.7%. The final reaction makes the smallest contribution (4.0%) in forming Al$_5$Cu$_2$Mg$_8$Si$_6$. Considering the solid fraction of fully solidified alloy, the Mg$_2$Si phases generated in the binary eutectic phase (Al + Mg$_2$Si) and the ternary eutectic phase (Al + Mg$_2$Si + Si) are concluded to be predominant intermetallic phase in this alloy. Thermo-Calc analyses are conducted under equilibrium solidification condition assuming that the cooling rate is slow enough to have full back diffusion in the solid phases. Therefore final microstructure of Al-8Zn-6Si-4Mg-2Cu alloys will have a composition corresponding to the end of the solidification process. Figure 3b shows that the main intermetallic compound existing in the final microstructure is Mg$_2$Si phases.

<table>
<thead>
<tr>
<th>Alloy Components</th>
<th>Zn</th>
<th>Si</th>
<th>Mg</th>
<th>Cu</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-8Zn-6Si-4Mg-2Cu</td>
<td>7.96</td>
<td>5.94</td>
<td>4.01</td>
<td>1.97</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>Al-8Zn-6Si-4Mg-2Cu-0.1Ti</td>
<td>7.95</td>
<td>5.98</td>
<td>3.98</td>
<td>1.96</td>
<td>0.13</td>
<td>Bal.</td>
</tr>
<tr>
<td>Al-8Zn-6Si-4Mg-2Cu-0.5Ti</td>
<td>8.01</td>
<td>5.98</td>
<td>4.03</td>
<td>1.99</td>
<td>0.49</td>
<td>Bal.</td>
</tr>
<tr>
<td>Al-8Zn-6Si-4Mg-2Cu-1Ti</td>
<td>7.99</td>
<td>6.02</td>
<td>4.02</td>
<td>2.01</td>
<td>1.02</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

**Table 1.** Chemical composition of different Ti additions to Al-8Zn-6Si-4Mg-2Cu alloys.
3.1. The Microstructure of the Al-8Zn-6Si-4Mg-2Cu Alloys Modified by Different Ti Additions

Table 2. The liquid and solid fractions for basic Al-8Zn-6Si-4Mg-2Cu alloy transition reaction.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Temperature (°C)</th>
<th>Liquid Fraction (%)</th>
<th>Solid Fraction (%)</th>
<th>Composition Percentage at Solid (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Al</td>
<td>582.8</td>
<td>100</td>
<td>0</td>
<td>Al - - Si - MgSi - Al5Cu2Mg8Si6</td>
</tr>
<tr>
<td>Start of binary</td>
<td>554.8</td>
<td>70.3</td>
<td>29.7</td>
<td>Al5Cu2Mg8Si6 - - MgSi - -</td>
</tr>
<tr>
<td>Start of ternary</td>
<td>539.7</td>
<td>48.6</td>
<td>51.4</td>
<td>MgSi - 95.2 - 4.8 - 4.8</td>
</tr>
<tr>
<td>Al5Cu2Mg8Si6</td>
<td>506.6</td>
<td>4.0</td>
<td>96.0</td>
<td>Al - 90.9 - 3.5 - 5.6 - -</td>
</tr>
<tr>
<td>506.6-8T</td>
<td></td>
<td></td>
<td></td>
<td>Mg - 89.8 - 3.3 - 4.2 - 2.7</td>
</tr>
</tbody>
</table>

Figure 3. Changes of liquid and solid fractions with temperature decrease during solidification process of Al-8Zn-6Si-4Mg-2Cu alloy (a), detailed diagram at solid fraction (b).

3.1. The Microstructure of the Al-8Zn-6Si-4Mg-2Cu Alloys Modified by Different Ti Additions

Figure 4. Shows various phases of Al-8Zn-6Si-4Mg-2Cu base alloys. As listed in Table 3 (EDS data), the gray matrix (marked as A in Figure 4) was α-Al and the black Chinese script phases (marked as B in Figure 4) were eutectic (Al + Mg2Si), the fibrous like phases (marked as C in Figure 4) were Si phases and the white particles (marked as D) were Al5Cu phases, and small gray particles (marked as E in Figure 4) were Al5Cu2Mg8Si6, respectively.

Figure 4. Scanning electron microscope (SEM) images of the Al-8Zn-6Si-4Mg-2Cu alloys.
Table 3. Energy dispersive spectrometry (EDS) analysis of the constituent phases in Figure 4 (atom fraction, at.%).

<table>
<thead>
<tr>
<th>Point</th>
<th>Chemical Composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>A</td>
<td>95.41</td>
</tr>
<tr>
<td>B</td>
<td>33.21</td>
</tr>
<tr>
<td>C</td>
<td>13.56</td>
</tr>
<tr>
<td>D</td>
<td>74.55</td>
</tr>
<tr>
<td>E</td>
<td>18.96</td>
</tr>
</tbody>
</table>

Microstructures of Al-8Zn-6Si-4Mg-2Cu alloys with and without the additions of Al-5Ti-1B master alloys were compared in Figure 5. Figure 5a,b are microstructures of unmodified Al-8Zn-6Si-4Mg-2Cu alloy which exhibits coarse eutectic Mg$_2$Si phases with Chinese-script morphologies (red arrow). Figure 5c,d shows microstructure of the same alloy after 0.1 wt.% Ti addition is made. From the microstructure, it was clear that a part of eutectic Mg$_2$Si was modified from Chinese script to polygonal morphology. More eutectic Mg$_2$Si was modified at 0.5 wt.% Ti addition, as shown in Figure 5e,f. The majority of the eutectic Mg$_2$Si still did not modify and Chinese-script type was still dominant. However, after 1 wt.% Ti addition was made, a dramatic result with a full modification in eutectic Mg$_2$Si, was observed as shown in Figure 5g,h. With the addition of 1 wt.% Ti, the size of eutectic Mg$_2$Si also decreases from over 50 µm to under 10µm, and the morphology of eutectic Mg$_2$Si transfers from Chinese script to polygonal shape. However, the Al-5Ti-1B master alloy does not affect the ternary eutectic phases. The effect of Al-5Ti-1B master alloy on grain refinement of aluminum alloys is well documented [14]. However, no significant changes in the grain size were observed in this study. According to Lee et al. [15], the effect of TiB$_2$ on grain size of aluminum alloy is negligible if the alloys contain more than 6 wt.% Si. The alloys used in this study contain 6wt.% Si or more. Therefore, it is considered that the grain size of primary aluminum is not affected greatly by the addition of Al-5Ti-1B, which is briefly estimated in the optical micrographs.

Figure 6a,b shows details of unmodified and modified eutectic Mg$_2$Si with the addition of 1 wt.% Ti. There are white particles (red arrow) in the modified eutectic Mg$_2$Si. The line scanning analysis of the Al-8Zn-6Si-4Mg-2Cu-1Ti alloy is shown in Figure 7. From the distribution of Ti, B, Mg and Si elements composition along the line crossing the modified eutectic Mg$_2$Si. B peak and Ti peak indicates that white particles are TiB$_2$ compound. The black particle is identified as Mg$_2$Si phase. From the distribution of elements, it is concluded that TiB$_2$ particles are located in the center of modified eutectic Mg$_2$Si as shown in Figure 7, which indicates that TiB$_2$ particles potentially acted as the nucleation site of the eutectic Mg$_2$Si.

In order to characterize those morphologies further, the Al matrix was removed by deep etching and the 3-dimensional morphologies of eutectic Mg$_2$Si are shown in Figure 5c,d. When comparing both SEM photographs, the morphological change of the eutectic Mg$_2$Si phase from dendritic Chinese script to angular polygonal shape is clearly demonstrated after the addition of TiB$_2$.

If the interface between the two phases has a good coherent relationship, they can act as heterogeneous nucleation sites for each other. The atomic arrangements should be similar in both crystal planes, and the interatomic distances difference also small [16]. TiB$_2$ crystal structure is hexagonal, and the lattice parameter is $a = 3.023$–$3.036$ Å, $c = 3.226$–$3.231$ Å [17]. Mg$_2$Si crystal structure is anti-fluorite, and the lattice parameter is $a = 6.36$ Å. During solidification of the Al-Ti-B system alloys, TiB$_2$ grows in the direction of $<001>$ and a surface of $[001]$ is exposed to the melt [17]. Chong reported that the disregistry at the interface between the (001) of TiB$_2$ and the (200) of Mg$_2$Si is $\sim$4.64% [12], which means that TiB$_2$ particles can be good heterogeneous nucleation sites for Mg$_2$Si.
Figure 5. Optical microscope images of the Al-8Zn-6Si-4Mg-2Cu alloys: (a,b) no Ti, (c,d) 0.1 wt.% Ti, 
(e,f) 0.5 wt.% Ti, (g,h) 1 wt.% Ti.
Figure 6. Microstructure of the eutectic Mg$_2$Si phases; (a) no modification; (b) modification; (c) no modification after deep etching; (d) modification after deep etching.

Figure 7. Line scanning analysis image of modified Mg$_2$Si phase of Al-8Zn-6Si-4Mg-2Cu-1Ti.

TiB$_2$ particles in Al-5Ti-1B master alloys are shown in Figure 8. Al-5Ti-1B master alloy is known to contain Al$_3$Ti and TiB$_2$ particles, and the TiB$_2$ particles are agglomerated (Figure 8b). When the amount of Al-5Ti-1B alloy was increased, TiB$_2$ particles in the master alloy also increased and can act as nucleation site for most eutectic Mg$_2$Si.
3.2. The Tensile Strength Change of Al-8Zn-6Si-4Mg-2Cu Alloys with the Addition of TiB₂

After addition of TiB₂ into the Al-8Zn-6Si-4Mg-2Cu alloy, the eutectic Mg₂Si changes from Chinese script to fine polygonal morphology as shown in Figure 5. Figures 9 and 10 show the effect of Ti content on yield strength (YS), ultimate tensile strength (UTS) and elongation (ε) to a fracture of Al-8Zn-6Si-4Mg-2Cu alloys. With 0.1 and 0.5 wt.% Ti addition, the mechanical properties are only slightly increased compared with the base alloys. However, the results indicate that when the Ti concentration increases from 0 to 1 wt.%, UTS is enhanced from 195 MPa to 253 MPa (30% improvement), YS increases from 175 MPa to 206 MPa (18% improvement), and elongation increases from 0.63% to 1.05% (66% improvement).

Micro-cracks are easily generated in intermetallic compounds, because of the stress concentration [18]. The small size and the polygonal shape of intermetallic compounds are preferable for the microstructure and it is clearly indicated that the marked increase in mechanical properties in this study is induced by the modification of eutectic Mg₂Si. Eutectic Mg₂Si, which was changed to a polygonal form with fine sizes of 5~10 μm, by adding 1wt.% Ti, can be the main reason for the mechanical properties improvement.

![Figure 8. SEM images of the Al-5Ti-1B master alloys (a), high resolution (b).](image)

![Figure 9. Stress-strain curve of Al-8Zn-6Si-4Mg-2Cu alloys with different Ti contents.](image)
1. The solidification process of the Al-8Zn-6Si-4Mg-2Cu alloy was estimated using Thermo-Calc software and it was found that the formation of eutectic Mg$_2$Si takes place around 554.8 °C. After the binary and ternary reactions, it is also confirmed that Mg$_2$Si is the predominant intermetallic phase in these alloys after solidification.

2. Mg$_2$Si morphology changed from Chinese script to polygonal, and the size decreased from over 50 μm to under 10 μm. The FE-SEM image exhibits TiB$_2$ particles inside the modified Mg$_2$Si. This suggests that TiB$_2$ particles acted as nucleation sites in modified eutectic Mg$_2$Si phases.

3. When 1 wt.% of Ti was added, most of the eutectic Mg$_2$Si phase was fully modified from large Chinese-script to a fine polygonal shape. The increase in the mechanical properties, both elongation and strength, were observed after modification of these large eutectic Mg$_2$Si phases.

4. Conclusions

In this paper, the phases of Al-8Zn-6Si-4Mg-2Cu alloy using thermodynamic computations was analyzed and confirmed by microstructure observation. The effect of Al-5Ti-1B master alloy on the microstructures and mechanical properties of Al-8Zn-6Si-4Mg-2Cu were investigated in this study. The following conclusions were drawn from the experimental results of this study.

1. The solidification process of the Al-8Zn-6Si-4Mg-2Cu alloy was estimated using Thermo-Cal software and it was found that the formation of eutectic Mg$_2$Si takes place around 554.8 °C. After the binary and ternary reactions, it is also confirmed that Mg$_2$Si is the predominant intermetallic phase in these alloys after solidification.

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