Effects of Titanium and Boron Additions with Cooling Rates on Solidification Behavior in Aluminum Alloys for Automotive Applications

JaeHwang Kim1,*, DongHoon Nam2, HooDam Lee2, KyungMoon Lee2, TaeGyu Lee2, HoonMo Park2 and Jongkook Lee2

1Gimje Special Casting & Forging Technology Support Center, Region Advanced Manufacturing Technology Agency, Korea Institute of Industrial Technology, 100, Jipyeongseosan-dong 3-gil, Baeksan-myeon, Gimje-si, Jeollabuk-do, 576-881, South Korea
2Research and Development Division, Hyundai Motor Group, 460-30, Sam-dong, Uihwag-Si, Gyeonggi-do, Korea

Al-Si based alloys are used to automobile parts for weight reduction. The engine block and chain cover were fabricated using the ADC12 and newly developed ADC12-M1 alloys through the high pressure die-casting. The ADC12-M1 alloy was fabricated by the addition of titanium and boron into the ADC12 alloy. Computational science such as JMatPro and Thermo-Calc was utilized in order to estimate the solidification behavior since the mechanical property of as-cast material is affected by the solidification behavior. The ADC12 and newly developed ADC12-M1 alloys belong to eutectic and hypo-eutectic alloys calculated by Thermo-Calc software, respectively. The cooling curves with the different cooling rates, fraction liquid and latent heat generation are estimated using JMatPro based on the Al-Si binary alloys in order to understand the solidification behavior between the eutectic and hypo-eutectic chemical composition. The cooling curves, fraction liquid and latent heat generation are more sensitive in the hypo-eutectic chemical composition than that in the eutectic one. The eutectic chemical composition is shifted into the higher concentration of silicon by the titanium and boron additions, resulting in that the higher difference of the yield strength is obtained in the hypo-eutectic ADC12-M1 alloy than that in the eutectic ADC12 alloy.

1. Introduction

Weight reduction of automobile becomes one of the most important things for the material development due to the improvement of fuel efficiency and reduction of CO2 emission. Lasa et al.1) and Chen et al.2) reported that Al-Si based alloys have been widely used for automobile parts such as connecting rods and engine blocks due to their good specific strength. Specially, yield strength of automobile part is regarded as important factor since the noise, vibration, and harshness (NVH) properties are strongly affected by the yield strength. Kumar et al.3) and Gao et al.4) found that grain refinement and solution hardening can be achieved by the titanium addition into Al-Si alloys. Tee et al.5) and Li et al.6) found that aluminum alloys are reinforced through the formation of the TiB2 particles by the both addition of titanium and boron. Yi et al.7) confirmed that TiB2 particles are effective for the enhancement of mechanical property. The present authors selected the titanium and boron as the additional elements to improve mechanical property of aluminum alloys for the application of the engine block and chain cover.

Computational science is utilized in this study to estimate the solidification behavior in the Al-Si based alloys. Simulation for the casting process is widely accepted for the new material and process development. Expecting the solidification behavior based on high quality data base is quite useful to develop casting material. Saunders et al.8) and Guo et al.9–11) reported that a computer program, Java-based materials properties (JMatPro), has developed an extensive database for the calculation of physical and thermo-physical properties such as molar volume, tensile strength, elastic modulus, fraction liquid, density and Poisson’s ratio. Sundman et al.12) and Andersson et al.13) reported that Thermo-Calc software is very useful tool which is based on the thermodynamic calculations. Lasa et al.14) and Cho et al.15) deduced the solidus temperature and predicted the solidification sequence in Al alloys using Thermo-Calc.

It is important to understand the effects of solidification behavior on the mechanical properties to develop the new material. However, it is hard to expect the solidification behavior and mechanical properties for the new material as long as there is no sufficient information of new material such as phase diagram. The goal of present study is therefore to understand the effects of solidification behavior on the mechanical properties based on the analysis of experimental and simulation results.

2. Experimental Procedure

Two kinds of material ADC12 and ADC12-M1 alloys were used in this study. The chemical composition of those alloys is given in Table 1. Pure aluminum with a purity of 99.8%, Al-10 mass% Ti and Al-5 mass% B master alloys were used in order to fabricate the titanium and boron added alloys. The alloys were melted at 750°C. The gas bubbling filtration (GBF) with a mechanical stirring of 600 rpm for 15 min was performed and the nitrogen gas was used. High pressure die casting with a pressure of 600 bar was performed. Figure 1 shows the automobile parts such as the engine block and chain cover which are fabricated using the ADC12 and ADC12-M1 alloys.

Table 1 Chemical composition of the used alloys [mass%].

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
<th>Ni</th>
<th>Fe</th>
<th>Mg</th>
<th>Sn</th>
<th>Ti</th>
<th>B</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC12</td>
<td>12</td>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.35</td>
<td>0.3</td>
<td>0.3</td>
<td>—</td>
<td>—</td>
<td>Bal.</td>
</tr>
<tr>
<td>ADC12-M1</td>
<td>12</td>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.35</td>
<td>0.3</td>
<td>0.3</td>
<td>5</td>
<td>1</td>
<td>Bal.</td>
</tr>
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*Corresponding author, E-mail: raykim@kitech.re.kr
ADC12-M1 alloy in this study. A same material was used for the both parts, but the thickness between engine block and chain cover is different. A thickness for chain cover is thinner compared to the engine block. Optical microscope (OM) was used to observe the as-cast microstructure. Etching solution using the solution of $\text{H}_2\text{O} + 0.5\% \text{H}$ was used in order to measure the grain size of $\alpha$-aluminum matrix. Tensile tests using MTS Electromechanical-300 kN were performed. The plate type of tensile test specimen was used with a gage length of 25 mm and a thickness of 3 mm. XRD patterns of the ADC12-M1 was recorded on a D8Advance (α1 System, Bruker) diffractometer where the 2 theta range was from 15 to 90° and the scan speed was 0.5°/min. Microstructure analyses to detect the strengthening phases formed by the titanium and boron additions were carried out using a JEOL equipment of JXA-8900R electron probe X-ray microanalyzer (EPMA). The diffraction pattern analyses for the structure of the strengthening phases such as AlTiSi and Al$_3$Ti phases were performed using JEM-2100F (JEOL) with an accelerating voltage of 200 kV and Technai G2 F30 S-TWIN (FEI) with an accelerating voltage of 300 kV.

3. Results

Figure 2 shows the microstructure of the chain cover and engine block, respectively. There are strengthening phases TiB$_2$ and Al$_3$Ti in the ADC12-M1 alloy as shown in Fig. 2(c). Emamy et al. explained that the TiB$_2$ particles are formed near the blocky Al$_3$Ti phase through the diffusion of boron atoms into the Al$_3$Ti particles. The strengthening phases such as TiB$_2$ and Al$_3$Ti phases are well distributed in the aluminum matrix. On the other hand, the eutectic silicon and primary silicon are confirmed in the ADC12 alloy. Much higher volume fraction of the $\alpha$-aluminum is confirmed in the ADC12-M1 alloy than that in the ADC12 alloy as shown in Fig. 2(c) and (d). From those microstructure comparisons, it
seems like that the chemical composition of the ADC12-M1 is closed to hypo-eutectic.

The XRD was performed in order to understand the newly formed phases for the as-cast material. Figure 3 shows the XRD result of the chain cover. The strengthening phases such as TiB$_2$, Al$_3$Ti and AlTiSi are confirmed in the ADC12-M1 alloy. The microstructure observation using EPMA was performed in order to distinguish the strengthening phases such as Al$_3$Ti, AlTiSi and TiB$_2$ phases. Figure 4 shows the EPMA results of the ADC12-M1 for the chain cover. Three kinds of phases such as Al$_3$Ti, AlTiSi and TiB$_2$ are confirmed. The observation of the microstructure with the different magnification was required since the size of TiB$_2$ particles is smaller than the other strengthening phases such as Al$_3$Ti and AlTiSi particles. TiB$_2$ particles are clearly distinguished from the AlTiSi and Al$_3$Ti particles since boron is contained only in the TiB$_2$ particles. Based on the EPMA results, AlTiSi particles are also distinguished from the Al$_3$Ti particles since the silicon is contained only in the AlTiSi particles. Further analysis, however, is required to distinguish the Al$_3$Ti and AlTiSi particles since the silicon can be detected from the eutectic silicon.

Figure 5 shows the diffraction patterns of the AlTiSi and Al$_3$Ti phases. The diffraction patterns of AlTiSi and Al$_3$Ti phases were obtained after checking the chemical composition by the Energy Dispersive X-ray Spectroscopy (EDX). Three diffraction patterns from the different zone axes were analyzed to clarify the structure of the AlTiSi phase. The d-spacing of 1-11, 200, 331 and 420 diffraction spot was measured to be 0.2253, 0.1934, 0.1396, 0.0929 and 0.0894 nm, respectively. The lattice parameter for this phase compares very well reported by Braun et al.\textsuperscript{17} The structure of the AlTiSi phase in this study is concluded as cubic structure based on the measurement of the plane spacing. In the case of Al$_3$Ti phase, the d-spacing of 200, -112 and 112 diffraction spot was measured to be 0.1990, 0.2387 and 0.2387 nm, respectively. The included angle was also measured to be 53.34° and 73.32° as described in Fig. 5. The lattice parameter for Al$_3$Ti phase, $a = b = 0.398$ nm, $c = 0.901$ nm, compares well reported by Liu et al.\textsuperscript{18} The structure of the Al$_3$Ti phase in this study is concluded as tetragonal structure.

Figure 6 shows the etched microstructure for the engine block and chain cover in the ADC12-M1 and ADC12 alloys. The partially distributed α-aluminum is selected to measure the grain size. The grain size of the α-aluminum in the ADC12-M1 alloy is 7.54 µm for the chain cover and 12.17 µm for the engine block, respectively. On the other hand, the grain size of the α-aluminum in the ADC12 alloy is 10.34 µm for the chain cover and 13.24 µm for the engine block, respectively. A similar grain size between the chain cover and engine block is obtained for the ADC12 alloy, but the smaller grain size of the chain cover is obtained than that in the engine block for the ADC12-M1 alloy. It is confirmed that the microstructure with the different cooling rates is more affected in the ADC12-M1 alloy than that in the ADC12 alloy based on the grain size measurement.

Figure 7 shows the yield strength for the chain cover and engine block in the ADC12-M1 and ADC12 alloys. The yield strength for the chain cover and engine block is similarly obtained in the ADC12. On the other hand, the yield strength of the engine block in the ADC-M1 alloy is lower than that of the chain cover. Generally, the thickness of the engine block is thicker than that of the chain cover. It is deduced that the different solidification behavior is caused by the cooling rate due to the different thickness of the automobile parts. It is noted that the ADC12-M1 alloy is more sensitive to the cooling rate than that in the ADC12 alloy. The details of those phenomena related to the solidification behavior in the hypo-eutectic and eutectic chemical composition with the different cooling rates are discussed in the next session.

4. Discussion

The different solidification behaviors between the ADC12-M1 and ADC12 alloys were confirmed. The different phenomena are caused by the titanium and boron additions...
Fig. 5 The diffraction patterns of AlTiSi phase (a), (b), (c) and Al$_3$Ti phase (d).

Fig. 6 The etched microstructure for engine block in the (a) ADC12-M1 and (b) ADC12 alloys and chain cover in the (c) ADC12-M1 and (d) ADC12 alloys, respectively.
into the ADC12 alloy. The present authors believe that the solidification behavior is basically caused by the different chemical composition and cooling rates during solidification. Recently, expectation of physical properties and phase diagram with a chemical composition based on computing science using JMatPro and Thermal-Calc. have been introduced in order to estimate the solidification behavior.

Figure 8 shows the expected phase diagram using Thermal-Calc. and simplified schematic diagrams for the ADC12 and ADC12-M1 alloys. Red arrows and blue dotted line as shown in Fig. 8 stand for the eutectic point of each alloy and the chemical composition of silicon used in this study, respectively. The eutectic point of the ADC12 alloy is closed to 12 mass% of silicon. On the other hand, the eutectic point of the ADC12-M1 alloy is closed to 15 mass% of silicon. Namely, the ADC12 and ADC12-M1 alloys belong to the eutectic and hypo-eutectic chemical composition. It is deduced that the solidification behavior of the ADC12 and ADC12-M1 alloys is similar with the Al-Si based eutectic and hypo-eutectic alloys, respectively.

4.1 Solidification behavior with the different cooling rates in Al-Si binary system

The different silicon amounts from 7 to 12 mass% were selected in order to understand the solidification behavior with the different cooling rates for the hypo-eutectic and eutectic chemical composition in Al-Si alloys. Figure 9 shows the expected cooling curves with the different silicon amounts and cooling rates in the Al-Si alloy using JMatPro. It is understood that the solidification is quickly completed with increasing the cooling rates. Moreover, the solidification is more quickly completed in the Al-7 mass% Si, hypo-eutectic chemical composition, than that in the Al-12 mass% Si, eutectic chemical composition regardless of the cooling rates. Figure 10 shows the expected fraction liquid with the different silicon amount in the Al-Si alloy using JMatPro. The temperature range of solidification is narrow with increasing the silicon contents. The fraction liquid is gradually decreased in the hypo-eutectic chemical composition. On the other hand, the fraction liquid is substantially decreased in the eutectic chemical composition. Figure 11 shows the expected latent heat with the different silicon
amount in the Al-Si alloy using JMatPro. The temperature range of heat evolution is also narrow with increasing the Si amounts. The difference of the solidification behavior with the cooling rates and the chemical composition is clearly confirmed in the hypo-eutectic and eutectic chemical composition in the Al-Si alloys.

4.2 Solidification behavior in ADC12 and ADC12-M1 alloys

The expected phase diagrams of ADC12 and ADC12-M1 alloys are obtained using Thermal-Calc. as shown in Fig. 8. It is confirmed that the ADC12-M1 and ADC12 alloys belong to the hypo-eutectic and eutectic alloys, respectively.
Figure 12 shows the cooling curves for the ADC12 and ADC12-M1 alloys calculated using JMatPro with the different cooling rates. The temperature decrease is faster in the ADC12-M1 alloy than that in the ADC12 alloy. It is deduced that the chemical composition of the ADC12-M1 alloy belongs to the hypo-eutectic alloy from the viewpoint of the cooling velocity comparison during the solidification.

Figure 13 shows the expected fraction liquid for the ADC12-M1 and ADC12 alloys using JMatPro. The fraction liquid becomes slowly decreased with decreasing the temperature until 566°C in the both ADC12-M1 and ADC 12 alloys. The fraction liquid of the ADC12-M1 and ADC12 alloys is 86 and 97% at the temperature of 566°C, respectively. Figure 14 shows the expected latent heat for the ADC12-M1 and ADC12 alloys using JMatPro. The heat evolution and the heat evolution range between the ADC12-M1 and ADC12 alloys is clearly different. The higher latent heat is generated in the ADC12-M1 alloy that in the ADC12 alloy. The temperature range of the latent heat generation, maximum temperature for the generated latent heat and generating latent heat energy at around the temperature of 566°C for the ADC12-M1 and ADC12 alloys are summarized in Table 2.

The reason for that the higher temperature of the latent heat generation appeared in the ADC12-M1 alloy than that in the ADC12 alloy is due to the formation of the solid phase at the higher temperature in the ADC12-M1 alloy compared to M1 and ADC12 alloys using JMatPro. The fraction liquid becomes slowly decreased with decreasing the temperature until 566°C in the both ADC12-M1 and ADC 12 alloys. The fraction liquid of the ADC12-M1 and ADC12 alloys is 86 and 97% at the temperature of 566°C, respectively. Figure 14 shows the expected latent heat for the ADC12-M1 and ADC12 alloys using JMatPro. The heat evolution and the heat evolution range between the ADC12-M1 and ADC12 alloys is clearly different. The higher latent heat is generated in the ADC12-M1 alloy that in the ADC12 alloy. The temperature range of the latent heat generation, maximum temperature for the generated latent heat and generating latent heat energy at around the temperature of 566°C for the ADC12-M1 and ADC12 alloys are summarized in Table 2.

Table 2 The expected temperature range of latent heat generation, maximum temperature for the generated latent heat and generating latent heat energy for the ADC12-M1 and ADC12 using JMatPro.

<table>
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<tr>
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<th>ADC12-M1</th>
<th>ADC12</th>
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<tr>
<td>Temperature range (°C)</td>
<td>470–740</td>
<td>475–620</td>
</tr>
<tr>
<td>Maximum temperature (°C)</td>
<td>740</td>
<td>620</td>
</tr>
<tr>
<td>Generating energy (J/g)</td>
<td>82.24</td>
<td>27.91</td>
</tr>
</tbody>
</table>

Figure 12 shows the cooling curves for the ADC12 and ADC12-M1 alloys calculated using JMatPro with the different cooling rates. The temperature decrease is faster in the ADC12-M1 alloy than that in the ADC12 alloy. It is deduced that the chemical composition of the ADC12-M1 alloy belongs to the hypo-eutectic alloy from the viewpoint of the cooling velocity comparison during the solidification.
the ADC12 alloy. Those different solidification behaviors between the ADC12 and ADC12-M1 alloys are confirmed using computer science such as Thermal-Calc. and JMatPro software.

The cooling curves, fraction liquid and latent heat were estimated in the Al-Si and ADC12 based alloys in order to understand the solidification characteristics for the hypo-eutectic and eutectic chemical compositions. The present authors believe that the different solidification behaviors are caused by the titanium and boron additions. Namely, the eutectic chemical composition is shifted into the higher concentration of silicon. Therefore, the similar phenomena during solidification between the Al-7 mass% Si and ADC12-M1 alloy are confirmed. Further researches to observe the microstructure and measure the mechanical properties and to describe the phase diagrams by the single addition of titanium or boron are required for the confirmative understanding about the solidification behavior.

5. Conclusions

Effects of the titanium and boron additions with the cooling rates on the solidification behavior are studied. Following remarks based on the experimental results and computing science expectation are drawn in this study.

(1) The strengthening phases such as Al3Ti, AlTiSi and TiB2 are formed by the titanium and boron additions into ADC12 alloy. The structure of the Al3Ti and AlTiSi phases based on the analyses of the diffraction pattern is concluded as tetragonal and cubic structure, respectively. The similar yield strength for the chain cover and engine block is obtained in the ADC12 alloy, but the yield strength in the engine block is lower than that in the chain cover in the ADC12-M1 alloy. Namely, ADC12-M1 alloy is more sensitive to the cooling rates.

(2) The chemical composition of ADC12-M1 and ADC12 alloys belongs to the hypo-eutectic and eutectic alloys based on Thermal-Calc. expectation. Temperature range of latent heat evolution broadened and maximum temperature and generated energy of the latent heat are increased in the ADC12-M1 alloy compared with the ADC12 alloy. The different solidification behaviors are mainly caused by the titanium and boron additions which shift the eutectic chemical composition into the higher concentration of silicon. The ADC12-M1 alloy belongs to the hypo-eutectic chemical composition through the comparison analyses such as the cooling curves, fraction liquid and latent heat evolution in the Al-Si and ADC12 based alloys based on the computational science estimation.

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REFERENCES