Effect of Mn Addition on the Age-Hardening Behavior of an Al-(9–10)%Si-0.3%Mg Die Casting Alloy in T5 and T6 Heat Treatment

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This study investigated the effect of Mn adding on the T5 and T6 age-hardening behaviors of Al-(9.0–10.0)%Si-0.3%Mg (equivalent to A360 alloy) and Al-10%Si-2%Cu-0.3%Mg (equivalent to A383 alloy) die casting alloys using a hardness measurement, an electron probe micro analyzer (EPMA) and thermodynamic software. When 0.4%Mn was added, the hardness of the T5 heat-treated Al-Si-Mg die casting alloy increases because the Mn addition suppresses the formation of the π-Al3FeMg2Si4 phase during solidification and distributes Mg into the α solid solution. This mechanism named as π-phase suppression mechanism promotes precipitation strengthening. In the T6 heat treatment, the hardness of the alloys hardly increased when Mn was added. In the Al-Si-Cu-Mg alloys, the hardening by the 0.5%Mn addition was negligible compared to that of the Al-Si-Mg alloys regardless of T5 or T6 treatment. Therefore, the hardening by Mn addition is the characteristic phenomenon in the T5 heat-treated Al-Si-Mg high-pressure die casting alloy.

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1. Introduction

Aluminum alloys for high-pressure die casting are used for automotive parts. For body parts, such as the main frame of motor cycles and suspension system of cars, higher ductility, toughness and strength compared to the conventional alloys are necessary. Winkelman et al. reported that Fe in aluminum die casting alloys tended to reduce soldering between the castings and the die1). Furthermore, Tsukuda et al. reported that ductility and toughness decreased with the formation of the platelet-like β-Fe intermetallic phase2). Nishi and Kami reported that Mn also showed an anti-soldering ability like Cu3). According to Seifeddine et al., increasing the Mn/Fe ratio suppresses the formation of the platelet-like β-Fe intermetallic phase and improves the tensile strength4).

For heat treatment, a T5 heat-treatment is used instead of T6 from the viewpoint of productivity and reduction of thermal strain. Inoue et al. reported the effect of pre-aging conditions on the hardness after the artificial aging of the T5 treatment for the Al-9%Si-0.3%Mg die casting alloy5). Ohtake et al. reported that the effect of the Mn addition on the pre-aging and T5 heat treatment behavior in the Al-9%Si-0.3%Mg alloys6). They indicated that the hardness after the T5 treatment increased with the addition of Mn. However, the reason of this hardening has not been clarified. In this study, the effect of Mn addition on the T5 age-hardening behavior of Al-(9–10)%Si-0.3%Mg (equivalent to A360 alloys) and Al-10%Si-2%Cu-0.3%Mg (equivalent to A383 alloys) die casting alloys were investigated.

2. Experimental Procedures

2.1 Alloy preparation and casting procedures

Al-Si-Mg and Al-Si-Cu-Mg alloys for high-pressure die casting with or without Mn addition (hereafter called AS, ASMn, ASC and ASCMn) were prepared. The chemical compositions of the alloys are listed in Table 1. The molten alloys (700 ± 5°C, melted in Ar atmosphere) were cast into a pure copper mold (25 ± 5°C). Figure 1 shows the dimensions of the casting. When the casting temperature decreased to 350°C, the casting was released from the mold and water quenched at 25 ± 5°C (cooling rate about 30°C/s).

2.2 Heat treatment

Heat treatment was performed with the following conditions on AS, ASMn, ASC and ASCMn.

T5 heat treatment: After water quenching, pre-aging for 0–4 d at room temperature, and artificial aging at 180°C for

Table 1 Chemical composition of alloys (mass%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si</th>
<th>Mg</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
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<tr>
<td>AS</td>
<td>10.1</td>
<td>0.28</td>
<td>&lt;0.01</td>
<td>0.15</td>
<td>&lt;0.01</td>
<td>Bal.</td>
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<tr>
<td>ASMn</td>
<td>9.3</td>
<td>0.30</td>
<td>&lt;0.01</td>
<td>0.14</td>
<td>0.42</td>
<td>Bal.</td>
</tr>
<tr>
<td>ASC</td>
<td>10.5</td>
<td>0.28</td>
<td>1.89</td>
<td>0.70</td>
<td>&lt;0.01</td>
<td>Bal.</td>
</tr>
<tr>
<td>ASCMn</td>
<td>10.4</td>
<td>0.29</td>
<td>1.88</td>
<td>0.70</td>
<td>0.45</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 1 Casting shape and dimensions (mm).
3 h.

T6 heat treatment: Solution heat treatment at 510°C for 4 h. after water quenching, artificial aging at 180°C for 3 h.

2.3 Rockwell hardness test
To investigate the effect of Mn addition and heat treatment on the hardness of AS, ASMn, ASC and ASCMn, hardness measurements were performed on the specimens using a Rockwell F scale hardness tester. The casting was cut into about 10 mm spacing, and was grind by using #800 emery paper. Figure 2 shows the cross section of the specimens and the positions of the indentation. After mean value, \( \mu \) and standard deviation, \( \sigma \) were calculated by using the measured hardness values from 8 indentations, the measured values outside the range of \( \mu \pm 2\sigma \) were omitted. This operation is to exclude the measured values outside of 95% confidential interval.

2.4 Micro Vickers Hardness test
To investigate the effect of the Mn addition and pre-aging time on the hardness of the primary \( \alpha \)-Al and the eutectic in AS and ASMn, hardness measurements were performed, avoiding Fe-based compounds, using the micro Vickers Hardness test, and a load of 0.049 N was applied for 10 s. The mean values were calculated from 14 indentation readings on 2 mm from the casting surface per specimen. After mean value, \( \mu \) and standard deviation, \( \sigma \) were calculated by using the measured hardness values from 14 indentations, the measured values outside the range of \( \mu \pm 2\sigma \) were omitted.

2.5 Qualitative, quantitative and area analyses using EPMA
To investigate the effect of the Mn addition and heat treatment on the microstructure, qualitative, quantitative and area analyses were performed using a JEOL JXA-8230 model electron probe micro-analyzer (EPMA) with a wavelength dispersive X-ray Spectrometer (WDS) for AS, ASMn, ASC and ASCMn. These analyses were performed to evaluate followings:
1. Change of Mg distribution to each constituent phase
2. Change of the kind of constituent phase
The quantitative analysis was performed on the primary \( \alpha \)-Al and eutectic of the alloys at 21 points, that is, 7 points per field of vision (256 \( \times \) 256 \( \mu \)m) \( \times \) 3 fields, and the mean value was calculated from the measurement results. ZAF correction was applied to the accumulated data. ZAF is a method to correct the factors (atomic number, absorption, fluorescence) which affect X-ray intensity.

2.6 Estimation of phase fraction
Thermodynamic analysis (JMatPro Version 8.00) were conducted to investigate the effect of the Mn addition on relationship between mass fraction of each phase and temperature from 500°C~600°C.

3. Result and Discussion

3.1 Al-Si-Mg alloys
3.1.1 Effect of the Mn addition on the T5 heat-treated alloys
Figure 3 shows the effect of the pre-aging time on the hardness of AS-T5 and ASMn-T5. Error bar in Fig. 3 shows the maximum and minimum values of the hardness of 8 indentations point. The hardness of AS-T5 and ASMn-T5 increases with pre-aging for 1 d, that is, the alloys show the positive effect, as shown earlier by Murakami7). The positive effect is defined as increase of the hardness by conducting pre-aging before artificial aging. Inoue et al. also reported that Al-Si-Mg alloys, which have similar composition to ASMn, exhibited the positive effect. Hence, Al-(9–10)%Si-0.3%Mg alloys exhibit the positive effect of pre-aging regardless of the Mn addition.

It is notable that the hardness increases by approximately 5 HRF due to the Mn addition regardless of pre-aging. To verify what phase contributed to the hardening, the micro Vickers hardness test was performed on primary \( \alpha \)-Al and eutectic microstructure of AS-T5 and ASMn-T5. Figure 4 shows that the hardness of the primary \( \alpha \)-Al and eutectic increased with Mn addition.

There are two possible reasons of the hardening of the primary \( \alpha \)-Al and the eutectic: (1) solid-solution strengthening by Mn and (2) promotion of precipitation strengthening.

First, to verify the possibility (1): the solid-solution strengthening by Mn, the age hardening curves without
pre-aging are shown in Fig. 5.

The hardness values of AS and ASMn without artificial aging are different by approximately 1 HRF. However, with artificial aging for 5 h, the difference increases to approximately 5 HRF. If solid-solution strengthening by Mn is the main cause of the hardening, the increase of the difference of HRF cannot be explained. Hence, the second possibility (2): the promotion of precipitation strengthening was suspected.

To verify the promotion of precipitation strengthening due to the Mn addition, EPMA(WDS) analyses were performed. Figure 6 shows the element mapping images of AS-T5 and ASMn-T5. From the analyses using EPMA and a report for Fe-rich intermetallic compounds in Al-11.5%Si-0.4%Mg (Cao and Cambell)\(^8\), the structure of AS-T5 consists of primary \(\alpha\)-Al, eutectic (\(\alpha\)-Al+Si), script-like \(\pi\)-Al\(_8\)FeMg\(_3\)Si\(_6\) phase (Fig. 7) and platelet-like \(\beta\)-Al\(_5\)FeSi phase\(^6\). The structure of ASMn-T5 consists of primary \(\alpha\)-Al, eutectic (\(\alpha\)-Al+Si), platelet-like AlFeMnSi phase, script-like \(\pi\)-Al\(_8\)FeMg\(_3\)Si\(_6\) phase and script-like AlFeMnSi phase.

The \(\pi\)-Al\(_8\)FeMg\(_3\)Si\(_6\) phase was observed in AS-T5 and ASMn-T5. It is well known that the presence of the \(\pi\) phase decreases the effect of precipitation strengthening. Caceres et al. reported that in Strontium-modified Al-7%Si-(0.4–0.7)%Mg alloys, the yield stress increased with increasing Mg content, although it is less than expected at 0.7% Mg due to the formation of \(\pi\) phase\(^9\). The phase that Fe, Mg and Si concentrate were the \(\pi\) phase. The phase that Fe, Mn and Si concentrate were the \(\alpha\)-Fe. It was found that the presence of the \(\pi\) phase in ASMn-T5 significantly decreased compared to that of AS-T5.

In AS and ASMn, the relationship between the content of each phase and the temperature was estimated using thermodynamics software JMatPro, as shown in Fig. 8. Table 2 shows the fraction of each phase of AS and ASMn at room temperature.

Similar to the analysis using EPMA, as shown in Fig. 8, the decrease of \(\pi\) phase was predicted by estimation using JMat-Pro.

Therefore, in AS-T5, during solidification, Mg in the molten alloy is consumed because \(\pi\) phase is formed. On the oth-
er hand, in ASMn-T5, the amount of consumption of Mg is smaller than that of AS, because the amount of π phase is smaller than that of AS. It is known that the precipitation sequence for a kind of Al-Si-Mg alloys such as A356 and/or A357 casting alloys starts with the formation of spherical GP zones consisting of an enrichment of Mg and Si atoms. The zones develop into a needle shaped coherent βz phase. Shivkumar et al. reported that the needles grow to become semi-coherent rods (β` phase) and finally non-coherent platelets (stable β phase (Mg2Si))\(^{10}\). Zhang and StJohn observed a large number of fine β` phase which had a diameter of 2–5 nm and a length of 10–20 nm in the peak-aged condition\(^{11}\). From the above, Mg contributes precipitation strengthening. Thus, the Mn addition promotes precipitation strengthening and increases the hardness because release of Mg which forms β` from the π phase. To confirm the release of Mg, the Mg concentration of primary α-Al and the eutectic of AS-T5 and ASMn-T5 was measured using EPMA(WDS), as shown in Table 3. Figure 9 shows the analysis points of quantitative analysis. The Mg concentration of both α phase in primary and eutectic of ASMn-T5 increased compared with that of AS-T5. Hence, Mn addition promotes precipitation strengthening as shown in Fig. 3. Because Mn addition suppresses the formation of π phase during the solidification and distributes Mg into the α solid solution.

### 3.1.2 Effect of Mn addition on the T6 heat-treated alloys

To investigate the effect of the Mn addition on AS-T6 and ASMn-T6, Rockwell hardness tests were performed. The hardness of AS-T6 and ASMn-T6 were 92.1 HRF and 92.9 HRF, respectively. When Mn was added, the hardness of the T6 heat-treated alloys hardly increased, whereas the hardness of the T5 heat-treated alloys increased by approximately 5 HRF. Figure 10 shows element mapping images of AS-T6 and ASMn-T6. The phase that Fe and Si concentrate were the β phase, the phase that Fe, Mn and Si concentrate was the α-Fe. Unlike the AS-T5, in AS-T6, π phase were not found regardless of whether Mn was added. Hence, solution treatment resolves π phase. Gustafsson et al. reported that in A356 alloys, by the T6 heat treatment, π phase was resolved and minute β` phase dispersed in the structure\(^{12}\). Elsharkawi et al. also reported that solution heat treatment caused a decrease in π phase in 356 and 357 alloys\(^{13}\). Therefore, in the T6 treatment, the suppression of π phase formation during solidification, which was found in the T5 treatment, did not occur because the π phase was resolved by the solution heat treatment. Then, Mg was distributed into the α solid solution regardless of the Mn addition.

### 3.2 Al-Si-Cu-Mg alloys

#### 3.2.1 Effect of Mn addition on the T5 heat-treated alloys

Figure 11 shows the effect of pre-aging on the hardness of ASC-T5 and ASCMn-T5. The hardness of ASC-T5 and ASCMn-T5 increased by approximately 1–2 HRF with pre-aging for 1 day. Al-10%Si-2%Cu-0.3%Mg alloys exhibited a slightly positive effect with pre-aging. When Mn was added, the hardness increased by approximately 2 HRF (ΔHRF = 2) regardless of pre-aging. The amount of increase (ΔHRF = 2) was smaller than that of the Al-Si-Mg alloys (ΔHRF = 5). In order to clarify the difference of ΔHRF between Al-Si-Mg

### Table 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>π phase</th>
<th>β-Fe</th>
<th>α-Fe</th>
<th>Mg2Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>0.0025</td>
<td>0.0044</td>
<td>-</td>
<td>0.0018</td>
</tr>
<tr>
<td>ASMn</td>
<td>0.00085</td>
<td>-</td>
<td>0.015</td>
<td>0.0024</td>
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### Table 3

<table>
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<tr>
<th>Alloy</th>
<th>primary α-Al</th>
<th>eutectic α-Al+Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>ASMn</td>
<td>0.09</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Fig. 7 π-AlFeMg3Si6 phase in AS, etch.0.5 HF, and Compo.

Fig. 8 Relationship between the content of each phase and the temperature calculated by JMatPro, (a) AS; (b) ASMn.

Fig. 9 Analysis points of quantitative analysis for Mg concentration of AS-T5 and ASMn-T5 in one of three fields.
alloys and Al-Si-Cu-Mg alloys, change of the precipitates or compounds by Mn addition in the Al-Si-Cu-Mg alloys was examined as follows. Many different precipitates in different combinations have been observed in the peak-aged condition of Al-Si-Cu-Mg alloys. Example of precipitates that can be present in the peak-aged condition are $\beta$ (Mg$_2$Si), $\theta$ (Al$_2$Cu) and $Q$ (Al$_5$Mg$_8$Si$_6$Cu$_2$) in Al-6.2%Si-3.8%Cu-0.45%Mg (Sjölander and Seifeddine)\textsuperscript{14}). From the analyses using EPMA and a report relating to Fe-rich intermetallic compounds in Al-11%Si-2%Cu-0.3%Mg (Panašková et al.)\textsuperscript{15}, the structure of ASC-T5 consists of primary $\alpha$-Al, eutectic ($\alpha$-Al+Si), Cu-rich phase (Fig. 12(a)), platelet-like $\beta$-Al$_4$FeSi phase (Fig. 12(b)) and script-like AlFeSi phase (Fig. 12(c)). The structure of ASCMn-T5 consists of primary $\alpha$-Al, eutectic ($\alpha$-Al+Si), Cu-rich phase (Fig. 12(a)) and script-like $\alpha$-$\text{Al}_{15}(\text{FeMn})_3\text{Si}_2$ phase (Fig. 13(b)). Cu-rich phase were mostly observed in notably eutectic-like structure. According to Tillova et al., the Cu-rich phase of this morphology are Al-Al$_2$Cu-Si in Al-9%Si-3%Cu-0.3%Mg alloy\textsuperscript{16}).

Figure 14 shows the element mapping images of ASC-T5 and ASCMn-T5. The phase containing both Fe and Si was the $\beta$-Fe. Mg and Cu are at almost identical positions, which were Al-Al$_2$Cu-Si phase, as shown in Fig. 12(a). The primary $\alpha$-Al and eutectic also contain Mg and Cu. However, other phase containing Mg and/or Cu, such as Q-Al$_5$Mg$_8$Cu$_2$Si$_6$ phase and Mg$_2$Si, were not observed using EPMA. In ASC and ASCMn, the relationship between the content of each phase and the temperature was estimated using thermodynamics software JMatPro, as shown in Fig. 15. Table 4 shows the fraction of each phase of ASC and ASCMn at room temperature. When Mn was added, the changes of mass fraction of each phase, such as $\pi$ phase, Q-Al$_5$Mg$_8$Cu$_2$Si$_6$ phase and Mg$_2$Si, were not observed except for the change from $\beta$-Fe to $\alpha$-Fe.

Therefore, when Mn was added, only the change of the Fe intermetallic compounds was found and the change in Mg- and/or Cu-rich phase was not found.

To investigate whether Mg and/or Cu was released when Mn is added, the Mg and Cu contents in primary $\alpha$-Al and eutectic in ASC-T5 and ASCMn-T5 were measured using EPMA(WDS), as shown in Table 5. The increase of Mg and Cu concentration was not found. Therefore, when Mn is added, the release of Mg and/or Cu does not occur because the Mg- and/or Cu-containing phase do not change. As a result, in the Al-Si-Cu-Mg alloys, the hardening because Mn addition was negligible compared with that of the Al-Si-Mg alloys.

3.2.2 Effect of Mn addition on the T6 heat-treated alloys

To investigate the effect of Mn addition on the hardness of the T6 heat-treated Al-Si-Cu-Mg alloys, Rockwell hardness tests were performed on ASC-T6 and ASCMn-T6. The hardness of ASC-T6 and ASCMn-T6 was 100.2 HRF and 100.6 HRF, respectively. Similar to the Al-Si-Mg alloys, hardening due to Mn addition was not found. No difference
was found except for the Fe intermetallic compounds. In the T5 treatment, Mg- and/or Cu-containing phase was observed. However, the phase was not found after the T6 treatment. Mn addition only changed the Fe-based compounds. Tilova et al. reported that Al-Al$_2$Cu-Si phase were gradually dissolved into the surrounding Al-matrix when the solution treatment time increased in Al-11%Si-2.5%Cu alloys$^{(17)}$. Similarly, in ASC-T6 and ASCMn-T6, Mg- and Cu-rich phase was resolved due to the solution treatment. When the solution treatment was applied, Mg and/or Cu was released. By Mn addition, it was only found that the $\alpha$-Al$_{15}$(FeMn)$_3$Si$_2$ phase appeared instead of $\beta$-Al$_5$FeSi phase. Hence, the $\pi$-phase suppression mechanism during solidification due to Mn addition was not identified.

### 4. Conclusions

In this study, the effect of Mn addition on the aging hardening behavior of the Al-(9.0–10.0)%Si-0.3%Mg alloys (equivalent to A360 alloy) and the Al-10%Si-2%Cu-0.3%Mg alloys (equivalent to A383 alloy) in T5 and T6 condition was investigated. The conclusions are as follows:

1. Regarding to the Al-Si-Mg die casting alloy, when 0.4%Mn was added, the hardness of the T5 heat-treated Al-Si-Mg alloy increased. Because Mn addition suppresses the formation of $\pi$ phase during solidification and distributes Mg into the $\alpha$ solid solution. This mechanism named as $\pi$-phase suppression mechanism promotes precipitation strengthening. However as to T6 treatment, Mn addition did not contribute to increase the hardness.

2. Regarding to the Al-Si-Cu-Mg die casting alloy, when 0.5%Mn was added, the hardening was negligible compared with that of the Al-Si-Mg alloy regardless of T5 or T6 treatment. Therefore, hardening due to Mn addition is the characteristic phenomenon of the T5 heat-treated Al-Si-Mg high-pressure die casting alloy.

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