Improvement of Strength–Elongation Balance of Al–Mg–Si Sheet Alloy by Utilising Mg–Si Cluster and Its Proposed Mechanism

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The tensile properties of an Al–Mg–Si alloy with Mg–Si clusters were compared with those of an Al–Mg–Si alloy with β′′ precipitates of the same strength. The elongation of the alloy with Mg–Si clusters was found to be greater than that of the alloy with β′′ precipitates because of the high work hardening rate of the former alloy, particularly in the high-strain region. Decomposition of Mg–Si clusters into solute Mg and Si atoms during the tensile deformation was revealed by differential scanning calorimetry. Transmission electron microscopy revealed three types of dislocation features in these alloys: homogeneous distribution of dislocations with β′′ precipitates, cell structures in the alloy with solute Mg and Si, and a combination of these two types in the alloy with Mg–Si clusters. In the case of the alloy with Mg–Si clusters, the yield strength increased significantly owing to the Orowan strengthening mechanism; simultaneously, the elongation of this alloy improved greatly because of the presence of solute Mg and Si atoms formed by decomposition via plastic deformation, which were inferred to prevent dynamic recovery in the later stage of tensile deformation. Consequently, a comparison of conventional 6000 series and 7000 series Al alloys revealed that the alloy with clusters had advantages over the alloy with precipitates and the alloy with solutes in terms of the balance between strength and elongation.

1. Introduction

An increase in both the strength and the elongation of sheet metal is favourable for improving its formability while maintaining strength. An inverse correlation is usually observed between formability and strength. It is therefore difficult to enhance both these properties simultaneously.

Lumley et al.1,2 reported that both the strength and the elongation of a wrought Al–Cu alloy can be increased simultaneously by forming the θ′ phase as well as the Guinier–Preston (GP) zone. Based on their work, Chen et al.3 reported that dislocations bypass the θ′ phase exiting the Orowan loops and shear the GP zones in this alloy. They considered that the increase in strength was due to the necessary force that was generated from the θ′ phase resisting dislocation motion, and they then suggested that the increase in elongation was due to the following two factors: (i) shearing of the GP zone by dislocations and its subsequent decomposition into solute Cu and other atoms during the later stage of deformation4 and (ii) an increase in the dislocation density brought about by the decomposed Cu atoms via an increase in the dislocation–dislocation junction strength, which, in turn, led to an increase in the work hardening rate5.

Mg–Si clusters are formed in Al–Mg–Si alloys after their aging at temperatures below 373 K6). Clusters are aggregates of Mg and Si atoms, and their crystal structures have been inferred to be the same as that of Al. This suggests that clusters may be sheared by dislocations and be decomposed into Mg and Si atoms, such as GP zones in an Al–Cu alloy. Clusters grow in size with increasing time of aging at their formation temperature7). An increase in the size of clusters can lead to an increase in their resistance force to dislocations. As a result, the yield strength of clusters can be expected to increase after long-term aging at the cluster formation temperature. However, thus far, no works have been conducted on the effects of cluster/precipitate size on the strength–elongation balance in Al–Mg–Si alloys.

In the present work, we investigated the effects of the cluster size after long-term aging at the cluster formation temperature on the balance between the strength and elongation of Al–Mg–Si alloys in order to clarify the mechanism of this balance.

2. Experimental

Table 1 lists the composition of the alloy used in the present study. Alloy sheets with a thickness of 4 mm were fabricated in a laboratory by casting, homogenization, and hot rolling. The sheets were subsequently cold-rolled to a thickness of 1 mm, subjected to solution heat treatment at 823 K for 1.8 ks using an air furnace, and quenched in ice water.
Finally, they were subjected to isothermal aging. In order to suppress natural aging after solution heat treatment, the as-quenched alloys were stored in liquid nitrogen until they were subjected to isothermal aging. Isothermal aging was performed in an oil bath at 373 and 453 K. Clusters and \( \beta'' \) precipitates were formed after isothermal aging at 373 K\(^6\) and 453 K\(^8\), respectively. To verify the influence of clusters on the strength and elongation of alloys with clusters, an alloy with \( \beta'' \) precipitates and an alloy with Mg and Si atoms in solid solution (an as-quenched alloy) were also prepared for comparison purposes.

A Vickers hardness measurement, tensile test, three-dimensional atom probe (3DAP) measurement, differential scanning calorimetry (DSC) measurement, and transmission electron microscopy (TEM) observation were conducted after each instance of isothermal aging. The Vickers hardness measurement was conducted using an MVK-G3 instrument (Akashi, Ltd., Japan) at room temperature (RT). Averages of values measured at five points, with an applied weight of 1 kgf on each sample, were used for further analysis. The relationship of the isothermal aging times at 373 and 453 K with the Vickers hardness value was obtained, and the target aging time at each temperature was determined for subsequent measurements.

The tensile tests were conducted using an Autograph AG-10TA tensile machine (Shimadzu, Japan) at room temperature. The specimens were cut from cold-rolled sheet into Japanese Industrial Standard (JIS) No. 5 specimens. Then, they were subjected to solution heat treatment followed by isothermal aging at 373 K and 453 K. The tensile direction was parallel to the rolling direction. The strain rate was 1 mm/min until a precise yield strength was obtained and it was thereafter increased to 10 mm/min.

Specimens for 3DAP measurements were carefully cut from the isothermally aged sheet to minimise strain. After being stretched under a given amount of strain, the tensile specimens were also subjected to TEM. Specimens for DSC measurements were cut from both the isothermally aged sheet and the subsequently stretched sheet with a nominal strain of 10%.

Finally, 3DAP (Oxford Nanoscience, Ltd., UK) measurements were performed. The needle specimen temperature for measurement was below 20 K. A total of 5,000,000 or more atoms were measured at more than two points in the same specimen. The average number of component atoms, the number density, and the Mg/Si atomic ratio in the Mg–Si clusters were evaluated from the 3DAP measurement data by the particle analysis method\(^7\) (maximum separation method). On the basis of our experience, we set two parameters—the fixed distance (\( d \)) and the minimum number of atoms (\( N \)) for particle analysis—as 0.8 nm and 20, respectively, for Mg and Si atoms. These values were set under the assumption that the detection rate of atoms in this apparatus was 35%.

Table 1. Alloy composition.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu (mass%)</th>
<th>Si (mass%)</th>
<th>Fe (mass%)</th>
<th>Mn (mass%)</th>
<th>Mg (mass%)</th>
<th>Zn (mass%)</th>
<th>Cr (mass%)</th>
<th>Ti (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05</td>
<td>0.81</td>
<td>0.16</td>
<td>0.05</td>
<td>0.65</td>
<td>0.01</td>
<td>0.04</td>
<td>0.01</td>
</tr>
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</table>

3. Results and Discussion

3.1 Strength and elongation after long-term aging

Figure 1 shows the Vickers hardness as a function of the isothermal aging time. The aging curve at 453 K—which is the temperature of formation of \( \beta'' \) precipitates—showed the maximum value of hardness (115 Hv) after aging for 7.2 ks, whereas the aging curve at 373 K—which is the temperature of formation of clusters—showed the same value of hardness after aging for 2160 ks. These results suggest that the strength of the alloy with clusters after long-term aging is comparable to that of the alloy with \( \beta'' \) precipitates. Tensile tests, 3DAP measurements, DSC measurements, and TEM observations were performed on specimens aged at 373 K—the temperature of formation of Mg–Si clusters—for 2160 ks and at 453 K—the temperature of formation of \( \beta'' \) precipitates—for 7.2 ks; all these tests, measurements, and observations were also performed on an as-quenched specimen after its solution heat treatment. The Vickers hardness of the as-quenched specimen was 46 HV.

Figure 2 shows a 3DAP elemental map of Mg and Si atoms obtained from an alloy aged at 373 K for 2160 ks, in which Mg–Si clusters formed. This figure clearly depicts the aggregates of Mg and Si atoms. The average number of Mg and Si atoms that constituted a Mg–Si cluster, the number density of the aggregates, and the average Mg/Si atomic ratio in the aggregates were determined to be 175 atoms, 3.2 \( \times 10^{24} \) m\(^{-3} \), and 0.56, respectively, by particle analysis. Some researchers in our group reported that 3DAP analysis of an alloy aged at 363 K for 2592 ks after solution heat treatment showed Mg–Si clusters with 120 atoms on average and a number density of 4 \( \times 10^{24} \) m\(^{-3} \). TEM diffraction analysis indicated that the crystal structure of the clusters was the same as that of Al metal\(^7\). Since the average number of atoms evaluated in the
The present study was similar to that reported in a previous study, it could be inferred that the aggregates of Mg and Si atoms observed in Fig. 2 were Mg–Si clusters.

The nominal stress and nominal strain curves of the as-quenched alloy, the alloy with Mg–Si clusters, and the alloy with β′′ precipitates are shown in Fig. 3, and their mechanical properties are listed in Table 2. The tensile strength of the alloy with clusters (364 MPa) was similar to that of the alloy with β′′ precipitates (348 MPa). On the other hand, the total elongation of the former alloy (22%) was greater than that of the latter alloy (15%). Consequently, an alloy with clusters has an advantage over an alloy with β′′ precipitates in terms of the balance between strength and elongation. The total elongation of the alloy with clusters (22%) was smaller than that of the as-quenched alloy (31%), whereas the strength of the former alloy was much greater than that of the latter alloy. Uniform elongations of the as-quenched alloy, the alloy with clusters, and the alloy with β′′ precipitates were 30%, 11%, and 9%, respectively. The corresponding local elongations of the three alloys were 1%, 11%, and 6%, respectively. The local elongation of the alloy with clusters was greater than those of the other alloys. A similar result was reported for an alloy with an Mg/Si content ratio of 2.10. The deviation of the observed values of strength and local elongation of the alloy with clusters from the general trend between them was considered to be a characteristic of this alloy. Although the details of these characteristics are unknown, it is notable that the alloy with clusters is favourable for metal products in which both uniform and local elongations are necessary for forming.

The true stress–strain and work hardening rate curves of the alloys as obtained from the nominal stress–strain curves in Fig. 3 are shown in Fig. 4. The point of intersection between the flow stress curves and the work hardening rate curves is defined as the point at which plastic instability commences. When the work hardening rate, dσ/dε, increases, this point moves towards the high-strain region. Therefore, the increase in the work hardening rate, denoted as dσ/dε, is inferred to correspond to the increase in elongation. The

![Fig. 2](image-url) 3DAP elemental maps of Mg and Si in alloy aged at 373 K for 2160 ks (52 nm × 55 nm × 103 nm). Mg and Si atoms are represented by blue and red circles, respectively.

![Fig. 3](image-url) Stress–strain curves of quenched alloy (A), alloy aged isothermally at 373 K for 2160 ks (B), and alloy aged isothermally at 453 K for 7.2 ks (C) after solution heat treatment in salt bath.

![Fig. 4](image-url) True stress–strain and strain hardening curves of quenched alloy (A), alloy aged isothermally at 373 K for 2160 ks (B), and alloy aged isothermally at 453 K for 7.2 ks (C) after solution heat treatment in salt bath.

![Fig. 5](image-url) DSC thermograms of quenched alloy (as-quenched) (a) and alloys aged isothermally at 373 K for 2160 ks without (b) and with 10% nominal tensile strain (c) after solution heat treatment.

<table>
<thead>
<tr>
<th>Mechanical properties of quenched alloy and alloys aged isothermally at 373 K (with clusters) and at 453 K (with precipitates) after solution heat treatment.</th>
<th>Yield Strength, YS/MPa</th>
<th>Tensile Strength, TS/MPa</th>
<th>Total Elongation (%)</th>
<th>Uniform Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-quenched</td>
<td>62</td>
<td>183</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>With clusters</td>
<td>293</td>
<td>364</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>With precipitates</td>
<td>325</td>
<td>348</td>
<td>15</td>
<td>9</td>
</tr>
</tbody>
</table>
ue of \( \frac{d\sigma}{de} \) at \( \varepsilon = 0.05 \) in both the alloy with clusters and the as-quenched alloy was 1050, and that in the alloy with \( \beta'' \) precipitates was 510. Notably, even in the high-strain region, the values of \( \frac{d\sigma}{de} \) in the alloy with clusters and in the as-quenched alloy remained higher than that in the alloy with \( \beta'' \) precipitates. Consequently, the fact that the elongations of the as-quenched alloy and the alloy with Mg–Si clusters were larger than that of the alloy with \( \beta'' \) precipitates is considered to be due to the difference in the work hardening in the high-strain region among these alloys.

### 3.2 Change in state of clusters during tensile deformation and development of dislocation structure

#### 3.2.1 DSC measurements

Figure 5 shows the DSC curves of alloys with clusters before and after 10% tensile deformation. The DSC curve of the as-quenched alloy is also shown for comparison. Previous reports on DSC measurements\(^7\) of an as-quenched specimen revealed the appearance of exothermic peaks in the following sequence: low-temperature cluster formation at 363 K, high-temperature cluster or \( \beta'' \) precipitate formation at 548 K, and \( \beta' \) precipitate formation at 593 K. Endothermic peaks appeared during low-temperature cluster dissolution at temperatures below 500 K. Based on previous reports\(^6,7,11\), we classified the clusters formed during aging at temperatures below 343 K as low-temperature clusters and the clusters formed during aging at temperatures above 343 K as high-temperature clusters. When aging was performed at 448 K, which corresponds to the temperature used for paint baking in automotive manufacture, high-temperature clusters grew into \( \beta' \) precipitates but low-temperature clusters did not\(^11\). This difference may be due to the difference in the structures of the clusters. However, no study has yet verified this observation. Results of DSC measurements reported in a previous paper\(^7\) reveal that the exothermic peaks at 363, 530, and 585 K for the as-quenched specimen as shown in Fig. 5(a) indicate the formation of low-temperature clusters, \( \beta'' \) precipitates, and \( \beta' \) precipitates, respectively. The endothermic peak at 494 K indicates the dissolution of low-temperature clusters, whose exothermic peak was at 363 K. Accordingly, the sequence of low-temperature cluster formation, its dissolution, \( \beta'' \) precipitate direct formation without accompanying high-temperature cluster formation, and \( \beta' \beta'' \) precipitate formation was detected in the heating period during the DSC measurement.

The DSC curve of the alloy without strain just after high-temperature cluster formation (Fig. 5(b)) shows that the exothermic peaks at 363, 530, and 585 K disappeared and a new exothermic peak appeared at 567 K; no such new exothermic peak was observed for the as-quenched alloy. We assumed that the endothermic peak observed at around 500 K was similar to the peak observed in an alloy with high-temperature clusters in a previous study\(^7\), although the origin of this peak remains to be understood. It was reported that when an Al–Mg–Si alloy was aged at 363 K for a long time following solution heat treatment, the exothermic peaks corresponding to the formation of low-temperature clusters and \( \beta'' \) precipitates decreased and the peak corresponding to the formation of \( \beta' \) precipitates shifted to a lower temperature\(^7\). The results of the DSC measurements in the present study are in good agreement with those in previous studies. Therefore, it is inferred that the high-temperature clusters formed after the treatment at 373 K for 2160 ks in the present study. Consequently, it is concluded that the peak at 585 K, which corresponds to the formation of \( \beta' \) precipitates, shifted to 567 K when the specimen with the high-temperature clusters was subjected to the DSC measurement. No exothermic peak was observed at around 530 K, which would have corresponded to \( \beta'' \) precipitate formation. This suggests that the already existing high-temperature clusters grew into \( \beta' \) precipitates without \( \beta'' \) precipitate formation during the DSC measurement.

The DSC curve obtained for the alloy with 10% tensile strain showed an exothermic peak at 530 K (Fig. 5(c)), whereas the DSC curve for the alloy without strain did not show this peak (Fig. 5(b)). This suggests that some high-temperature clusters decomposed into solute Mg and Si atoms during tensile deformation, and then, these atoms formed the \( \beta'' \) precipitates during the DSC measurement. Irrespective of the tensile deformation after the formation of high-temperature clusters, no exothermic peak existed at 585 K (Figs. 5(b) and (c)) corresponding to the heat of reaction generated from the formation of \( \beta' \) precipitates from \( \beta'' \) precipitates during the DSC measurement; however, the exothermic peak at 585 K was seen in the DSC curve of the as-quenched alloy (Fig. 5(a)). Accordingly, the exothermic peak at 530 K observed in the DSC curve of the alloy after 10% tensile deformation following heat treatment for high-temperature cluster formation was postulated to be due to the high-temperature cluster formation during the DSC measurement. This suggests that during tensile deformation of the alloy with the high-temperature clusters, some clusters decomposed into solute Mg and Si atoms, but others continued to remain and act as nuclei of the high-temperature clusters, which could grow during the DSC measurement. A small exothermic peak at 363 K, which reflects the formation of low-temperature clusters, was observed in this alloy as well as in the as-quenched alloy. This indicates that some Mg–Si clusters decomposed into solute atoms owing to the tensile deformation and formed low-temperature clusters at 363 K during the DSC measurement.

The change in the state of GP zones in an Al–Cu alloy was directly observed by 3DAP measurements in such a manner that the GP zones were sheared by dislocations and then decomposed into solute atoms\(^8\). In the present study, we attempted to perform 3DAP observations of an Al–Mg–Si alloy with high-temperature clusters. However, 3DAP data could not be obtained, because the needle specimen inevitably fractured. Nevertheless, the results of the DSC measurements of the Al–Mg–Si alloy suggest that the high-temperature clusters decomposed into solute Mg and Si atoms through being sheared by dislocations, as has been reported to occur in the GP zones in an Al–Cu alloy.

#### 3.2.2 TEM observation of development of dislocation structures during tensile deformation

Figures 6–8 show TEM micrographs of the dislocation structures after 10% tensile deformation of the specimens of a) an as-quenched alloy (Fig. 6), b) an alloy isothermally aged at 373 K for 2160 ks (Fig. 7), and c) an alloy isothermally aged at 453 K for 7.2 ks (Fig. 8), following solution heat treatment. Figure 6 shows the clear cell structure of the dislo-
cations developed in the as-quenched alloy. In the alloy with high-temperature clusters (Fig. 7), the dislocations were distributed more homogeneously than they were in the as-quenched alloy; however, the cell structures were occasional-

ly observed to appear as those indicated by the broken circles. On the other hand, in the alloy with $\beta''$ precipitates (Fig. 8), the dislocations developed homogeneously without forming cell structures, and a majority of them were pinned by the $\beta''$ precipitates.

### 3.2.3 Interaction between clusters and dislocations

The results of the DSC measurements suggest that during tensile deformation, high-temperature clusters decompose into solute Mg and Si atoms. The diffusion distance of both atoms after decomposition is presumed to be relatively short because only a few atomic vacancies exist in the high-temperature clusters. Therefore, we consider that both the decomposed atoms exist near the clusters. As mentioned in section 3.2.2, a homogeneous dislocation structure developed after 10% tensile deformation in the alloy with high-temperature clusters as well as in the alloy with $\beta''$ precipitates, whereas cell structures developed in the as-quenched alloy. These results indicate the following: 1) high-temperature clusters act as obstacles to dislocation motion and increase the yield strength; then, the dislocations are distributed homogeneously; 2) tensile plastic deformation partly decomposes these clusters into solute Mg and Si atoms by means of dislocation; and 3) solute atoms promote the formation of the cell structure of dislocations. The alloy with high-temperature clusters as well as the as-quenched alloy had a high work hardening rate in the high-strain region (Fig. 4). Such a high work hardening rate was due to the decomposition of clusters into atoms which suppressed the dynamic recovery in the high-strain region. On the other hand, it was observed that in the alloy with $\beta''$ precipitates, the dislocations were pinned by the precipitates, resulting in uniformly and densely distribut-
ed dislocations without the formation of cell structures. This shows that the resistance to dislocation motion in the alloy with $\beta''$ precipitates was greater than that in the alloy with clusters and that in the as-quenched alloy, leading to the high yield stress in the alloy with $\beta''$ precipitates. Such a high density of dislocations can be dynamically recovered during the later stages of deformation. This explains the greater yield strength of the alloys with $\beta''$ precipitates than of the as-quenched alloy, as well as the lower elongation of the former alloy than of the latter alloy.

The cell structures observed in the alloy with high-temperature clusters and in the as-quenched alloy are believed to be a result of the rearrangement of the dislocations following their cross slip. Akiyoshi et al.\textsuperscript{12} observed cross slip of dislocations in an Al–Mg–Si alloy at 2% nominal strain by TEM. Kinoshita et al.\textsuperscript{13} demonstrated the promotion of cross slip by the strain field around very fine precipitates in $\alpha$-Fe by a molecular dynamics method. In face-centred cubic metals, following cross slip, dislocations become sessile through in-
teractions among themselves\textsuperscript{14}, and such sessile dislocations and other dislocations produce cell structures during subse-
due to the formation of sessile dislocations following cross slips. The occurrence of cross slip in the high-strain regions needs to be investigated in the future. In the case of the alloy with high-temperature clusters,
we concluded that solute Mg and Si atoms formed through the decomposition of clusters during plastic deformation induced the formation of some cell structures and that the dynamic recovery was suppressed. The decomposition of clusters is considered to maintain the high work hardening rate even in the high-strain region.

### 3.3 Strength–elongation balance of Al alloys

Figure 9 shows the strength–elongation balance of alloys in the present study as well as those in the conventional 6000 series and 7000 series. The alloy with high-temperature clusters clearly has an advantage over other alloys in terms of the strength–elongation balance. Accordingly, it is concluded that this alloy has the potential to exhibit a greater balance than previously observed.

### 4. Conclusion

The effects of the state of Mg and Si in Al–Mg–Si alloys, such as solute Mg and Si, Mg–Si clusters, and β′′ precipitates, on their strength–elongation balance were investigated. The findings of the study are summarised as follows.

(1) The strength of the alloy aged at 373 K—which is the temperature of formation of Mg–Si clusters—for 2160 ks was similar to the maximum strength obtained for the alloy aged at 453 K—which is the temperature of formation of β′′ precipitates—for 7.2 ks. Elongation of the former alloy was greater than that of the latter alloy. In addition, the work hardening rate of the former alloy was higher than that of the latter alloy, particularly in the high-strain region.

(2) The DSC measurements suggest that the clusters were presumably sheared by dislocations, leading to the decomposition of clusters into solute Mg and Si. The Mg–Si clusters increased the yield strength significantly by acting as obstacles to dislocation motion. In the high-strain region, solute Mg and Si atoms improved the strength–elongation balance by suppressing the dynamic recovery.

(3) TEM observations after 10% tensile deformation of the alloy with solute Mg and Si atoms showed cell structures, whereas those after 10% tensile deformation of the alloy with β′′ precipitates showed homogeneously distributed dislocations pinned by the β′′ precipitates. In the alloy with Mg–Si clusters, combinations of cell structures and homogeneously distributed dislocations, i.e. cell structures that had developed mainly in the region of homogeneously distributed dislocations, were observed. This supports the hypothesis of the decomposition of Mg–Si clusters into solute Mg and Si atoms during tensile deformation.

### Acknowledgments

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