Morphology and Crystallography of β-Mg$_2$Si Precipitation in Al–Mg–Si Alloys

Yasuya Ohmori, Long Chau Doan*, Yoshitsugu Matsuura*, Sengo Kobayashi and Kiyomichi Nakai

Department of Materials Science and Engineering, Ehime University, Matsuyama 790-8577, Japan

The exothermic reaction occurring after β’ precipitation in Al–Mg–Si alloys has been investigated by means of differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The reaction peak height observed in DSC increases with increasing excess Mg or decreasing excess Si content from Al-Mg$_2$Si quasi-binary composition. It was confirmed that this reaction peak arises from the precipitation of cuboid β-Mg$_2$Si particles related to the matrix with the cube-cube orientation relationship. At the later stage of ageing, thin β-Mg$_2$Si plates nucleate at the cuboid β-phase particles. The orientation relationship of them is rotated 45° or 18.4° in the further aged specimens about the direction normal to the $\{001\}_{\beta}$ $\parallel$ $\{001\}_{\beta}$ habit plane from the cube-cube relationship. The changes in morphology and the crystallography of the β-Mg$_2$Si precipitates with the progress of ageing can be explained qualitatively in terms of coherency and interface energy of the precipitates.

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1. Introduction

It has been commonly believed that the decomposition of supersaturated Al–Mg$_2$Si quasi-binary alloys occurs in the following sequence: the formation of solute atom clusters, the precipitation of β’ needles, the precipitation of metastable β’-rods and the precipitation of equilibrium β-Mg$_2$Si plates.$^{1,2}$

In the differential scanning calorimetry (DSC) curves for these alloys, a sharp and large exothermic peak can be observed in the temperature range between 250 and 300°C. This reaction is due to the needlelike β’ precipitation$^{1,3,4,6–8}$ producing extremely large hardening. The exothermic reaction following subsequently after the β’’ formation has been interpreted as the transformation of β’’ needles to β’ rods and B’ particles,$^{9}$ and various structural models for β’$^{2,4,6,10–13}$ and B’$^{14}$ phases have been proposed. Although DSC is quite sensitive to detect the reactions occurring, it is rather difficult to identify the each reaction peak as the formation of the phase observed by transmission electron microscopy (TEM). This is because TEM observation has been carried out mostly on the isothermally aged specimens. The direct correspondence between DSC and TEM results in the specimens with exactly the same heat histories has been examined by Edwards et al.,$^9$ but such cases are still quite scarce. Thus, it is difficult to obtain a positive evidence indicating that the exothermic reaction peak following the β’’ formation arises truly from the transformation of β’’ needles to β’ rods.

The aim of the present study, therefore, is to examine closely the reaction detected by DSC subsequently after the β’’ needle formation by means of DSC and TEM.

2. Experimental Procedures

The chemical compositions of the Al–Mg–Si alloys used in the present study are shown in Table 1. The alloys 1 to 3 contain excess Mg atoms from quasi-binary Al–Mg$_2$Si compositions, the alloy 4 is a quasi-binary alloy and the alloys 5 to 8 are those of excess Si. The ingots with the dimensions of 25 × 35 × 150 in mm were homogenised at 560°C for 12 h in air and were rolled into 1 mm thick plates. The plates were machined into various shapes suitable for DSC and microstructure examination. These specimens were placed in evacuated quartz tubes, solution-treated at 560°C for 30 min and quenched into iced water. DSC measurements were carried out by a Rigaku differential scanning calorimeter. As a reference sample, high purity aluminium annealed at 560°C for 1 h was used. The heating rates examined were 10, 20, 30 and 50°C/min. The blank effect was subtracted from the result obtained for the alloy sample as conducted by Jena et al.$^{15}$ The slope of the base line and the base line calibrations were also carried out.

In order to prepare thin foils for transmission electron microscopy, the solution treated specimens were aged at constant heating rates up to appropriate temperatures. Isothermal ageing at various temperatures was also conducted. Thin foils were prepared by a conventional twin-jet polishing technique using a 20 vol% perchloric acid ethanol solution and were observed in JEM 2000EX microscope operated at 200 kV.

Table 1 Chemical composition of Al–Mg–Si alloy (at%).

<table>
<thead>
<tr>
<th>Mark</th>
<th>Mg</th>
<th>Si</th>
<th>Mg$_2$Si</th>
<th>Excess Si</th>
<th>Excess Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 1</td>
<td>1.30</td>
<td>0.38</td>
<td>1.14</td>
<td>-0.27</td>
<td>0.54</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>1.48</td>
<td>0.48</td>
<td>1.44</td>
<td>-0.26</td>
<td>0.52</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>1.32</td>
<td>0.42</td>
<td>1.26</td>
<td>-0.19</td>
<td>0.48</td>
</tr>
<tr>
<td>Alloy 4</td>
<td>0.82</td>
<td>0.47</td>
<td>1.23</td>
<td>0.06</td>
<td>-0.03</td>
</tr>
<tr>
<td>Alloy 5</td>
<td>1.23</td>
<td>0.79</td>
<td>1.85</td>
<td>0.17</td>
<td>-0.09</td>
</tr>
<tr>
<td>Alloy 6</td>
<td>1.20</td>
<td>0.90</td>
<td>1.80</td>
<td>0.30</td>
<td>-0.60</td>
</tr>
<tr>
<td>Alloy 7</td>
<td>0.88</td>
<td>0.85</td>
<td>1.32</td>
<td>0.41</td>
<td>-0.21</td>
</tr>
<tr>
<td>Alloy 8</td>
<td>0.93</td>
<td>1.03</td>
<td>1.39</td>
<td>0.57</td>
<td>-0.29</td>
</tr>
</tbody>
</table>

*Graduate Student, Ehime University.
3. Experimental Results

3.1 DSC measurements

Figure 1 shows the examples of DSC curves at 50°C/min. In the excess Si Alloy 7, eight reactions were detected, i.e., six exothermic reactions A, B, D, E, F and G, and two endothermic reactions C and H. Within these reactions, it has been well established that a sharp exothermic reaction D arises from the precipitation of $\beta''$ needles. A relatively small reaction peak E can be recognized subsequently after the reaction D, and has been interpreted as the transformation of $\beta''$ needles to $\beta'$ rods and $B'$ phase so far.9) The purpose of the present study is to examine the reaction E in detail. The peak height of the reaction D increased and the peak temperature lowered with increasing excess Si content. This behavior indicates that the excess Si content accelerated the precipitation of $\beta''$ needles. It should, however, be noted that the peak height of the reaction E decreased with increasing excess Si content. As described later in TEM observation, the transformation from $\beta''$ needles to $\beta'$ rods increased with increasing excess Si content. Thus, the peak height E would have increased with increasing Si content if the reaction E were the transformation of $\beta''$ needles to $\beta'$ rods. The effect of heating rate on the peak height of the reaction E is also of interest. In the excess Mg alloy, it was as high as that of D at 50°C/min as in Fig. 1. With decreasing heating rate to 20°C/min, however, the peak height of the reaction D decreased significantly in comparison with that of D as in Fig. 2. In the excess Si alloy 6, two peaks D and E were clearly separated because the temperature for the reaction E decreased with increasing excess Si content.

In order to assess the relative peak height for the reactions D and E, $h_E/h_D$ was plotted against excess Si content as in Fig. 3. Here, $h_D$ and $h_E$ are referred to as the peak heights for the reactions D and E, respectively. The $h_E/h_D$ ratios exhibited relatively high values in the excess Si content less than 0.2%, but the drastic decrease to about 0.3 due to increasing excess Si content was observed in the excess Si range between 0.2 and 0.3%. It is also interesting to note that the $h_E/h_D$ ratio increased significantly with the increase of heating rate.

3.2 TEM observations

Figure 4 illustrates the $\beta''$ needles lying along (100)$_{Al}$ matrix directions observed in the excess Si alloy 6 aged up to 275°C at 20°C/min just above the reaction D peak. The bright field image and the selected area electron diffraction pattern are shown in Figs. 4(a) and (b), respectively. The reflections from the precipitates are highly streaked in the directions parallel to (100)$_{Al}$ and were difficult to analyse the structure directly from these patterns. In the excess Mg alloy 1 aged up to 300°C at 50°C/min, $\beta''$ needlelike precipitates were also observed as shown in Fig. 5.

Since the peak height ratio $h_E/h_D$ increases with increasing excess Mg content, the precipitates formed in the reaction E will be more easily found in the excess Mg specimens aged up to the temperature where the reaction E has just completed. Figure 6 shows the microstructure of the excess Mg alloy 3 aged up to 330°C at 20°C/min just above the reaction E peak. The bright field image, the selected area electron diffraction pattern and the key diagram for it are in Figs. 6(a), (b) and (c), respectively. Dispersion of fine cuboid particles as small as about 17 nm can be recognised in addition to $\beta''$ needles, the surfaces of cuboidal particles being parallel to [100]$_{Al}$ matrix planes. These particles accompanied strong coherent strain fields around them. The reflections other than those from the Al matrix can be indexed as those from $\beta$-Mg$_2$Si and the double reflections between the precipitates and the matrix are indicated by open circles. The reflections from the needlelike precipitates ($\beta''$) could not be obtained in this case. This is because the amounts of $\beta''$ needles decreased and cuboid $\beta$
Fig. 4 Fine β" needles in the excess Si alloy 6 aged up to 275°C at 20°C/min. (a) The bright field image and (b) the selected area electron diffraction pattern.

Fig. 5 Fine β" needles in the excess Mg alloy 2 aged up to 300°C at 50°C/min.

particles increased in number. The diffraction pattern (b) and its analysis (c) indicate that the cuboid β-Mg$_2$Si particles are related to the matrix by the cube-cube orientation relationship:

[100]$_\beta$ || [100]$_{Al}$, [010]$_\beta$ || [010]$_{Al}$, [001]$_\beta$ || [001]$_{Al}$

Kanno et al. have already reported the formation of such cuboid precipitates, but have not identified them to be β-Mg$_2$Si. All the examinations carried out on the excess Mg and the quasi-binary Al-Mg$_2$Si alloys indicate that the reaction E detected in DSC arises from the formation of cuboid β-Mg$_2$Si particles. Figure 7 is an example in a different matrix orientation. The zone axis was parallel to the [111]$_{Al}$ direction. As can be seen in the bright field image (a), the shape of the precipitates appears as if they are hexagonal. This can be understood by the fact that the projection of a cuboid particle with [100] surfaces forming on a [111] plane is hexagonal. The orientation relationship between β-Mg$_2$Si and the Al matrix is also that of cube-cube as in Figs. 7(b) and (c). In the excess Si alloy aged up to the temperature where the reaction E completed, the precipitates were still mostly needlelike and
the diffraction spots obtained were aligned on the lines of the streaks due to $\beta''$ needles. The formation of cuboid $\beta$-Mg$_2$Si particles could not be confirmed in this ageing condition because the amounts of $\beta$-Mg$_2$Si particles were much less than those in excess Mg alloys as can be seen in DSC results and also it was difficult to distinguish the fine cuboid particles from the cross sections of $\beta''$ needles. However, since the formation of cuboid $\beta$-Mg$_2$Si particles in the excess Si alloys was also confirmed in the isothermally aged specimens as described later, it is likely that the reaction E arises from the cuboid $\beta$-Mg$_2$Si formation.

In the excess Mg alloy 2 isothermally aged at 245°C for 5 h, $\beta''$ needles and fine cuboid $\beta$ particles were observed simultaneously as shown by arrows A and B in Fig. 8, respectively. This was confirmed by the dark field illumination using a reflection from $\beta$ phase. The average size of $\beta$ particles was as small as 15 nm. The diffraction pattern from the precipitates indicates that the $\beta$ precipitates are related to the matrix by the cube-cube orientation relationship. Prolonged holding at 300°C, the formation of $\beta$-Mg$_2$Si plates in addition to the cuboid particles was recognised. Figure 9 shows a platelike precipitate nucleating at cuboid $\beta$-Mg$_2$Si particles in the excess Mg alloy 3 aged at 300°C for 20 h as indicated by arrows. The bright field image, the selected area electron diffraction pattern and the schematic representation are in Figs. 9(a), (b) and (c), respectively. The average size of cuboid $\beta$-Mg$_2$Si particles was almost the same as that observed in Fig. 6, but the platelike precipitate was much larger than the cuboid particles. The diffraction pattern (b) comprised the reflections from both cuboid and platelike precipitates. The analysis of the pattern (c) indicates that the platelike precipitate is also $\beta$-Mg$_2$Si and is related to the matrix in the relationship reported by Kanno et al.:

\[
\begin{align*}
[100]_{\text{Al}} & \parallel [1\bar{1}0]_{\beta}, [010]_{\text{Al}} \parallel [110]_{\beta}, \\
(001)_{\text{Al}} & \parallel (001)_{\beta} \cdots \text{habit plane}
\end{align*}
\]

This relationship can be obtained by 45° rotation about the [001]$_{\text{Al}}$ parallel to [001]$_{\beta}$ axis from the cube-cube relationship, the habit plane of the plate being parallel to the (001)$_{\text{Al}}$ parallel to (001)$_{\beta}$ plane. In the excess Mg alloy aged at 300°C for 50 h, another type of platelike $\beta$-Mg$_2$Si was formed as shown in Fig. 10. The bright field image (a) revealed that the plate is much larger than that in Fig. 9. The diffraction pattern (b) and its analysis (c) indicate that this platelike precipitate is also $\beta$-Mg$_2$Si phase and is related to the matrix by the following orientation relationship:

\[
\begin{align*}
[100]_{\text{Al}} & \parallel [310]_{\beta}, [010]_{\text{Al}} \parallel [\bar{1}30]_{\beta}, \\
(001)_{\text{Al}} & \parallel (001)_{\beta} \cdots \text{habit plane}
\end{align*}
\]

This relationship can be obtained by 18.4° rotation about the [001]$_{\text{Al}}$ parallel to [001]$_{\beta}$ axis from the cube-cube relationship.

In the excess Si alloy 8 aged isothermally at 245°C for 10 h, the precipitation of fine cuboid $\beta$-Mg$_2$Si particles in addition
The precipitation of $\beta$ plates and cuboid particles in the alloy 1 aged at 300°C for 20 h. (a) The bright field image, (b) the selected area electron diffraction pattern, and (c) the schematic representation of (b).

The density of $\beta''$ needles was quite high in comparison with that in the excess Mg alloys, identification of individual $\beta$-Mg$_2$Si particles was rather difficult as in Fig. 11(a). A close examination of the image, the diffraction pattern (b) and its analysis (c), however, indicates that the fine cuboid $\beta$-Mg$_2$Si particles exhibit the cube-cube relationship with the matrix precipitated as indicated by arrows. By ageing at 245°C for 180 h, the $\beta$-Mg$_2$Si plates with the orientation relationship reported by Kanno et al. were also observed in the excess Si alloy 8. The bright field image, the selected area electron diffraction pattern and its schematic representation are shown in Figs. 12(a), (b) and (c), respectively. As indicated by an arrow in (a), the plate was observed as a square with about 70 nm sides. The diffraction pattern (b) and its analysis (c) showed that the orientation of the $\beta$-Mg$_2$Si plate is rotated 45° about $[001]_A \parallel [001]_{\beta}$ axis from the cube-cube relationship.

4. Discussions

The reaction E in the DSC study has been interpreted as the transformation of $\beta''$ needles to $\beta'$ rods or $B'$ phase so far. The present TEM observation, however, confirmed that this exothermic peak arises from the formation of fine cuboid...
Fig. 11. Precipitation of $\beta''$ needles and fine $\beta$ particles in the alloy 8 aged at 245°C for 10h. Arrows indicate fine cuboid $\beta$-$\text{Mg}_2\text{Si}$ particles. (a) The bright field image, (b) the selected area electron diffraction pattern, and (c) the schematic representation of (b).

$\beta$-$\text{Mg}_2\text{Si}$ particles nucleating separately from $\beta''$ needles, i.e., the transformation of $\beta''$ needles to either $\beta'$ or some other precipitates does not occur in the reaction E but the cuboid $\beta$ particles precipitate. This interpretation for the reaction E is also supported by the fact that the $\beta$-$\text{Mg}_2\text{Si}$ cubes are easily found in the Al-Mg-Si alloys with small excess Si contents. Although the detection of cuboid $\beta$-$\text{Mg}_2\text{Si}$ particles was difficult in the excess Si alloys when continuously heated, the cuboid $\beta$ particles, which were nucleated separately from $\beta''$ needles, were also recognised in the isothermally aged specimens after the $\beta''$ needle formation.

It is of interest that the morphology and the crystallography of $\beta$-$\text{Mg}_2\text{Si}$ particles change with the progress of ageing. At the initial stage of $\beta$-$\text{Mg}_2\text{Si}$ precipitation where the supersaturation of solute atoms is large, the nuclei of the precipitates will be formed in the Si and Mg enriched regions by the rearrangements of the matrix lattice as small as possible. In order to understand the crystallography of the $\beta$-$\text{Mg}_2\text{Si}$ precipitation, the atomic arrangements on the $(001)_{\text{Al}} \parallel (001)_{\beta}$ plane for the three cases observed are shown in Fig. 13. The lattice parameters for Al and $\beta$-$\text{Mg}_2\text{Si}$ were assumed to be 0.405 and 0.635 nm, respectively. In the case of the cube-cube orientation relationship, although some excess atoms are present in the matrix, the inter-planar distance for three successive
[200]_{AI} planes correspond to that of two [200]_{β} planes as can be seen in Fig. 13(a). Thus, the matrix lattice should expand linearly about 4.5% to precipitate β phase if the coherency at the precipitate/matrix interfaces are kept. This is a small misfit and it is likely that the cube-cube relationship is chosen at the early stage of the coherent nucleation of β-Mg_{2}Si phase particles. It should also be mentioned that the cube directions in cubic materials are elastically soft. This will support the precipitation of cuboid β-Mg_{2}Si particles. On the other hand, since the unit cell volume of Al, 0.4053 nm³, and that of β-Mg_{2}Si, 0.6353 nm³, contain four and twelve atoms respectively, the volume increment due to β-phase precipitation is about 28.5%, the linear expansion being 8.7%. Thus, the excess atoms should be removed from the matrix if the coherency is kept at the interfaces during the nucleation of β phase particles. In addition to it, the coherent strain will increase and the concentration of solute atoms in the matrix will decrease with the growth of these particles. Such effects will reduce the driving force for the precipitation of cuboid β-Mg_{2}Si particles in the cube-cube orientation relationship.

Then, the interface energy will control the further progress of precipitation. It is interesting to note that the atomic arrangements on the (001)_{AI} matrix are quite similar to those on the (001)_{β} β-Mg_{2}Si planes in the orientation relationship reported by Kanno et al. as shown in Fig. 13(b), i.e., the relationship rotating the [010]_{β} direction 45° from the [010]_{AI} direction about the [001]_{AI} || [001]_{β} direction. Although the dimensional misfit for the β-phase precipitation along the [100]_{AI} or [010]_{AI} direction is significantly large, i.e., 10.86% expansion, this misfit can be completely compensated by introducing a misfit dislocation for every nine (220)_{β} atomic planes of β-phase. Thus, the (001)_{AI} || (001)_{β} plane in this orientation relationship with misfit dislocations will be one of planes with very low geometrical interface energy. On the other hand, since the misfits normal to this plane are large, the precipitates suitable for this condition will be in a platelike shape. It is therefore likely that the β-Mg_{2}Si particles forming at this stage is platelike with the (001)_{AI} || (001)_{β} habit plane. These β-Mg_{2}Si plates nucleate at cuboid β-Mg_{2}Si particles and grow into the size much larger than cuboid β-Mg_{2}Si particles. Further ageing for long time, the formation of β-Mg_{2}Si plates showing a different orientation relationship with the matrix has been confirmed in the present study. The orientation relationship between β-Mg_{2}Si and the matrix was rotated about 18.4° from the cube-cube relationship about the [001]_{AI} || [001]_{β} direction. In this case, although the atomic arrangements on this plane are not so good in comparison with those in the relationship reported by Kanno et al., the near coincident site lattice is formed as shown in Fig. 13(c) and the dimensional misfits on this plane will be extremely small. Since the atomic arrangements on the planes normal to this plane is also not so good, the shape of β-Mg_{2}Si particles will be platelike. Therefore, at the final stage of ageing, this type of precipitation will predominate.

5. Conclusions

The exothermic reaction occurring after the β″ precipitation has been examined in the excess Mg, the Al–Mg_{2}Si quasi-binary alloys and the excess Si alloys by means of DSC and TEM, and the following results were obtained.

1. The exothermic reaction E which follows the β″ precipitation increases with increasing excess Mg content or reducing excess Si content.

2. In the excess Mg specimens aged continuously up to the temperature where the reaction E completed, the separate nucleation of fine cuboid β-Mg_{2}Si particles can be observed.

3. Although the peak height ratio of this reaction against that of β″ precipitation in DSC decreases with increasing Si content, the formation of cuboid β particles can be clearly recognised after the β″ precipitation in the excess Si specimens isothermally aged.

4. Thus the reaction E is not due to the transformation of β″ needles to β′ rods as so far believed but arises from the separate nucleation of cuboid β-Mg_{2}Si particles related to the matrix with the cube-cube orientation relationship.

5. At the following stage of ageing, there is a formation of thin β-Mg_{2}Si plates rotated 45° and also 18.4° about the direction normal to the (001)_{AI} || (001)_{β} habit plane from the cube-cube relationship.

6. The changes in morphology and the crystallography of the β-Mg_{2}Si precipitates with the progress of ageing can
be explained in terms of misfit strain and interfacial energy of the precipitates.

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