Ageing Processes in Al–Mg–Si Alloys during Continuous Heating

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The precipitation behaviours during continuous heating in the Al–Mg2Si alloys with excess Mg and Si contents have been investigated by means of Vickers hardness measurements, differential scanning calorimetry and transmission electron microscopy. The first exothermic reaction occurring at the lowest temperatures is due to the annihilation of quenched-in vacancies by the collapse of vacancy clusters and the migration of vacancies to various sinks such as grain boundaries. The prismatic dislocation loops formed by this collapse are frequently observed. The second reaction detected as broad hardening increases with increasing excess Si content and can be interpreted as the formation of solute atom clusters. The sharp and large exothermic reaction inducing the largest hardening corresponds to the precipitation of β′-Mg2Si particles. The formation of β′ and Type-B rods can be recognised in the quasi-binary and the excess Si at slightly higher temperatures.

(Received September 13, 2001; Accepted December 13, 2001)

Keywords: aluminium–magnesium–silicon alloy, precipitation, β″ needles, β′-Mg2Si particles, β′ rods, Type-B precipitates, crystallography, transmission electron microscopy

1. Introduction

The precipitation sequence in solution-treated Al–Mg2Si alloys has been reported as: clustering of Si and Mg atoms → needlelike β″ precipitation → transformation of β″ needles to β′ rods → stable platelike β′-Mg2Si precipitation. Kanno et al. demonstrated that cuboid fcc particles with the lattice parameter a = 0.633 ± 0.005 nm precipitate in the (α + Mg2Si) 2 phase region as a transient phase from β′ rods to β′-Mg2Si plates. Westengen and Ryum also observed similar cuboid particles and concluded that they are of equilibrium β′-Mg2Si phase from the energy dispersive X-ray analysis. In the excess Si alloys, however, Matsuda et al. reported a hexagonal Type-A phase with a = 0.405 and b = 0.670 nm, an orthorhombic Type B phase with a = 0.684, b = 0.793 and c = 0.405 and a hexagonal Type-C phase with a = 1.05 and b = 0.405 nm form. The precipitation of β′′ and β′ phases has been studied extensively and various models for the crystal structures have been proposed, i.e., monoclinic structures for β″ needles, hexagonal structures for β′ rods. Thus, further detailed study will be necessary to specify the structures.

It should also be noted that the precipitation sequence has often been examined by differential scanning calorimetry (DSC) during continuous heating and that the results have been compared in many cases with those obtained by transmission electron microscopy (TEM) for the isothermally aged specimens. The processes in continuous heating, however, will be significantly different from those in isothermal ageing.

The purpose of the present study is, therefore, to clarify the effects of excess Si and Mg on the ageing behaviour during continuous heating by means of DSC, TEM and Vickers hardness measurements, systematically.

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

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Si</th>
<th>Mg2Si</th>
<th>Excess Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 1</td>
<td>1.48</td>
<td>0.48</td>
<td>1.44</td>
<td>-0.26</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>0.82</td>
<td>0.47</td>
<td>1.23</td>
<td>0.06</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>1.23</td>
<td>0.79</td>
<td>1.85</td>
<td>0.17</td>
</tr>
<tr>
<td>Alloy 4</td>
<td>0.88</td>
<td>0.85</td>
<td>1.32</td>
<td>0.41</td>
</tr>
<tr>
<td>Alloy 5</td>
<td>0.93</td>
<td>1.03</td>
<td>1.39</td>
<td>0.57</td>
</tr>
</tbody>
</table>

2. Experimental Procedures

The chemical compositions of the materials used are shown in Table 1. The ingots were homogenised at 833 K for 12 h and were rolled to 1.25 mm thick plates at room temperature. The disklike specimens 1.25 mm thick and 5 mm in diameter were machined from the plates for DSC, TEM and hardness measurements. They were solutionized at 833 K for 30 min and quenched into iced water. Immediately after quenching, DSC measurements were carried out at constant heating rates between 10 and 50 K/min in a dynamic N2 atmosphere to minimise the oxidation following the procedure by Jena et al. The specimens for Vickers hardness measurements and TEM observation were also aged to various temperatures in the same specimen holder of the differential scanning calorimeter. The heating rates for all the specimens were exactly the same. The hardness and TEM specimens were cooled in a dynamic N2 atmosphere after reaching the temperatures. Micro-Vickers hardness measurements were conducted with 300 g load. Thin foils for TEM were prepared by electrolytic polishing in the mixture of three parts of methanol and one part of HNO3 at 243 K and were examined in a JEOL-2000EX microscope operating at 200 kV.

3. Experimental Results

3.1 Vickers hardness measurements

Figures 1(a) and (b) show the effects of continuous heating temperature on Vickers hardness for the heating rates of 10
and 50 K/min, respectively. The materials used are the excess Mg (Alloy 1), the quasi-binary (Alloy 2) and the excess Si alloys (Alloy 5). In the case of heating at 10 K/min, all the specimens exhibited a similar hardening sequence as can be seen in Fig. 1(a), i.e., slight hardening at temperatures between 350–425 K (this hardening will be referred to as “PH1”), and small softening at temperatures around 450 K, and a sharp and large hardening at temperature around 550 K (PH2) with the subsequent large drop in hardness. The reaction temperatures displaced to higher temperatures with increasing heating rate as shown in Fig. 1(b). The hardness of the excess Si alloy was much higher than that of the quasi-binary alloy aged at temperatures below PH2 but the hardness increment was much reduced in the over-aged condition. In the present study, although the hardness of the excess Mg alloy decreased in comparison with that of the quasi-binary alloy, Suzuki et al. reported that the excess Mg alloy quenched after complete solutionising induces hardness higher than that of the quasi-binary alloy. Such difference may arise from the incomplete solution treatment, because the chemical composition of this alloy was in rather critical region. The peak temperature of PH2 was lowered considerably with increasing excess Si content.

On these figures, the temperatures where the small exothermic reaction A were detected by DSC measurement were superposed. Although the heating rates for both DSC and hardness measurements were exactly the same, some additional ageing might have progressed in the hardness specimens during the cooling in a dynamic N2 atmosphere. This implies that the true temperatures for the hardness peaks should be displaced to higher temperature sides. It should be noted that, even in such situations, the peak temperatures for the first slight hardening, PH1, are clearly separated from those of the reaction A (DSC-A) as can be seen in Fig. 1. Thus, the mechanisms inducing these two reactions may be different.

### 3.2 DSC results

As examples, DSC thermograms at various heating rates from 10 to 50 K/min in the alloys 2 and 5 are shown in Figs. 2(a) and (b), respectively. The peak temperatures for PH1 and PH2 were superposed also on these figures. By examining all the DSC curves, four exothermic reactions, i.e., A, C, D and E, and two endothermic reactions, B and F, were recognised. In the DSC curves for the quasi-binary alloy 2, a diffuse exothermic peak A, an endothermic peak B, a large and sharp exothermic peak C, the following significantly large exothermic peak D, a diffuse peak E and a broad endothermic peak F can be observed, the peak temperature being displaced to higher temperatures by increasing heating rate from 10 to 50 K/min as shown in Fig. 2(a). It should be noted that the PH1 deviates significantly from the peak A to higher temperature side as pointed out in Fig. 1. The PH2 temperature is in good agreement with that for the peak C.

Since the peak height ratio of the reaction D to that of C, hD/hC, is thought to be roughly proportional to the ratio for the amounts of the reactions, hD/hC was plotted against excess Si content (Fig. 3). The hD/hC ratio decreased drastically with increasing excess Si content above 0.2%. Thus the reaction D may be predominant in the low excess Si alloys.

The area of each peak calibrated by heating rate provides the enthalpy change directly relating to the molar heat and the

![Fig. 1](image1.png)

**Fig. 1** Effects of heating temperature on Vickers hardness. Heating rate: (a) 10 K/min and (b) 50 K/min.

![Fig. 2](image2.png)

**Fig. 2** DSC curves for Alloys 2 and 5 heated at different rates: (a) Alloy 2 and (b) Alloy 5.
volume fraction of precipitation or dissolution. The effects of excess Si content on the enthalpy changes for the reactions A and C are shown in Fig. 4(a). These enthalpy changes increased with increasing Si content. The enthalpy change for the reaction A increased from 1.9 to 3.8 J/g and that for the reaction C varied from 4.5 to 9.9 J/g with increasing the excess Si contents from $-0.26$ to $0.57$ at%. The activation energies for the reactions were calculated by Kissinger method:

$$\ln \frac{T_i^2}{\Phi} = \frac{Q^*}{RT_i} + \ln \frac{Q^*}{Rk_0}$$

Here, $T_i$ is the peak temperature for a reaction, $\Phi$ is the heating rate, $R$ is the gas constant, $k_0$ is the pre-exponential factor and $Q^*$ is the activation energy of the reaction. Since the last term in the above equation can be approximated as a constant, the activation energy $Q^*$ can be obtained from the slope of $\ln(T_i^2/\Phi)$ against $1/T_i$. The fraction decomposed, $Y$, can be described by Johnson-Mehl-Abrami equation as:

$$Y = 1 - \exp(-\beta^n).$$

Here

$$\beta = \int_{T_i}^{T_f} k_r(T) dT$$

and

$$k_r = k_0 \exp(-Q^*/RT).$$

Figure 4(b) shows that the excess Si does not affect on the activation energies for the reactions A and C. The activation energies for the diffuse exothermic reaction A are in the range from 52.3 to 64.5 kJ/mol but those for the sharp exothermic reaction C are in the ranges from 100.8 to 118.8 kJ/mol.

### 3.3 TEM observations

The TEM images of the specimens aged to the peak temperatures for the reaction A are shown in Fig. 5. Figures 5(a) and (b) are the weak beam dark field image using the $\langle 111 \rangle_A l$
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ection for the excess Si alloy 5 aged to 348 K at 10 K/min and the bright field image for the excess Mg alloy 1 aged to 390 K at 50 K/min, respectively. In the excess Si specimen, many small dotlike contrasts can be seen as in Fig. 5(a) as indicated by small arrows. It is likely that these contrasts arose from the Frank-type edge dislocation loops formed by the collapse of vacancy clusters on the \{111\}_Al planes. In the excess Mg specimen, much larger dislocation loops were observed as shown in Fig. 5(b). The difference in loop size between two specimens may arise from either the maximum heating temperature or the chemical composition. These dislocation loop contrasts were very sensitive to heating temperature, difficult to observe in the specimens aged to the peak temperature of diffuse hardening, PH1, and could never be observed in the specimens aged to the temperatures where the endothermic reaction B completed.

Figure 6 shows very fine needlelike precipitates formed by heating at 50 K/min to 573 K, the peak temperature for the reaction C in the excess Si alloy 5. The bright field image and the selected area electron diffraction pattern are in Figs. 6(a) and (b). The reflecting zone axis was close to the [031]_Al and very fine needles elongated in (100)_{Al} directions and dotlike contrasts can also be recognised in Fig. 6(a). These dotlike contrasts arose from the cross sections of the needles elongating into the direction normal to the foil. The diffraction spots from the needlelike precipitates were largely elongated as often reported for \( \beta'' \) phase, the directions of the streaks being normal to the \( \langle 100 \rangle_{Al} \) needle directions. Although the well defined reflections from \( \beta'' \) needles could be obtained in the specimens isothermally aged for long time at temperatures below 523 K, only the streaks were observed in the continuously heated specimens. This may arise from the facts that the precipitating phases change before \( \beta'' \) needles grow large enough to produce the well defined reflections during continuous heating.

In order to reveal the effects of chemical composition on the reaction D, the fine structures in the excess Mg alloy 1 were examined first. Figure 7 shows the TEM image for the excess Mg alloy 1 aged to 553 K at 10 K/min, where the reactions C and D were overlapped. The bright field image, the selected area electron diffraction pattern with its analysis are in Figs. 7(a), and (b), respectively. The reflecting zone axis is parallel to the [001]_Al matrix direction. Fine particles with the average size of 10–20 nm can be recognised as well as \( \beta'' \) needles. The diffraction pattern and its analysis indicate that the fine particles are of \( \beta \)-phase relating to the Al matrix with the cube-cube orientation relationship, i.e., \((100)_{\beta} \parallel (100)_{Al}, (010)_{\beta} \parallel (010)_{Al}\), as reported previously. In the specimen aged to 635 K at 50 K/min, \( \beta'' \) needles disappeared almost completely and only cuboid \( \beta \) particles were recognised.

In the case of the quasi-binary alloy 2 aged at 50 K/min...
to 635 K where the reaction D has nearly completed, cuboid β particles much coarser than those in the excess Mg alloy were observed as well as fine β″ needles. The number of the β particles, however, decreased significantly in comparison with that in the excess Mg alloy. Figures 8(a) and (b) are the bright field image in the [¯41¯1]Al zone axis and the selected area electron diffraction pattern with its analysis. The cuboid particles were confirmed to be β phase as shown in Fig. 8(b). The surfaces of the cubes appeared to be parallel to the {100}Al matrix planes as reported previously. 7, 9, 24) Very fine needles lying parallel to ⟨100⟩Al directions are probably of β″ phase although the diffraction pattern from them could not be obtained due to small density of the precipitates in this area. In a different area of the same specimen, however, a much coarse rodlike precipitate with the average diameter of 15 nm was observed occasionally as indicated by an arrow in Fig. 9(a). The diffraction pattern and its analysis in Fig. 9(b) indicates that the rodlike precipitate is of hexagonal β′ phase determined by Jacobs. 2) The orientation relationship between the β′ rod and the matrix can be expressed as:

\[(021)_β \parallel (013)_{Al}, \ (012)_β \parallel (031)_{Al}, \ (100)_β \parallel (100)_{Al} \]

• growth direction

This relationship is rotated 8° about the [100]β || [100]Al axis from the cube-cube relationship, i.e., the separation angle between (021)β and (013)Al is about 8°. Although this rotation from the cube-cube relationship is relatively small, it may not be an experimental error. This is because β particle would have taken a cuboid morphology if the isotropic cube-cube relation held between it and the matrix. In the same specimen, β′ and Type-B rods were frequently recognised. The bright field image of a β′ rod indicated by an arrow and the selected area electron diffraction pattern with its analysis are in Figs. 11(a) and (b), respectively. The orientation relationship be-
Fig. 10 β particles formed by heating to 635 K at 50 K/min in the excess Si alloy 5. (a) The bright field image and (b) the selected area electron diffraction pattern with its analysis.

Fig. 11 Precipitation of β′ rods in the excess Si alloy 5 aged at 50 K/min to 635 K. (a) Bright field image and (b) the selected area electron diffraction pattern with its analysis.

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4. Discussion

In order to clarify the ageing processes during continuous heating, three points described below should be noted.

(1) The first slight hardening peak (PH1) does not coincide with the exothermic peak A and deviates about 50–80 K to one another.

(2) The peak height ratio of the reaction D to the reaction C decreases with increasing excess Si content, and at this ageing stage cuboid β particles precipitate predominantly in excess Mg and low excess Si alloys.

(3) In the excess Mg specimen heated continuously to 635 K at 50 K/min, only the dispersion of cuboid β particles is observed. In the quasi-binary specimen of the same ageing condition, β′ rods precipitate in addition to β′′ and β particles. In the excess Si specimen, the precipitation of Type B rods was also observed. The precipitation of Type A and C rods, however, could not be recognised in the present continuous heating experiments.

The first exothermic reaction A has been interpreted as the formation of solute atom clusters so far.1,4,33) It should, however, be pointed out that this temperature is much lower than the broad hardening peak (PH1) which is thought to be the solute atom cluster formation. In the specimens aged to the temperature where the reaction A was detected, however, the contrasts arising probably from prismatic dislocation loops were observed as shown in Fig. 5. It is also likely that the excess vacancies are dissipated by forming vacancy clusters as well as by migrating to some sinks such as grain boundaries. Suzuki et al.23) reported that such dislocation loops are difficult to observe in the Al–Mg–Si alloys aged at 448 K for 10 min. This may arise from the facts that the loops can be observed in quite narrow temperature range during continuous heating and also those in the excess Si alloys are very small in size. The subsequent migration of solute atoms to the prismatic dislocation loops will eliminate the loops, leading to the formation of solute atom clusters. These solute atom clusters are also difficult to observe by TEM as reported by Suzuki et al.32) In fact, according to our unpublished work, the isothermal ageing at 448 K for 10 min corresponds to the initial stage of β′′ precipitation where such loops can never be observed. The exothermic heat and the activation energy for the reaction A are in the ranges from 1.9 to 3.8 J/g and 52.3 to 64.5 kJ/mol, respectively, as shown in Fig. 4. In 6061 alloys, Dutta et al.4) reported that this activation energy is 33.1 kJ/mol, but Doan et al.33) determined the enthalpy change and the activation energy as 1.3 J/g and 79 kJ/mol, respectively. The activation energies obtained in the present alloys are, therefore, in-between of the values described above.4,33) These values are much smaller than those for the bulk diffusions of Al, Si and Mg atoms in Al matrix, i.e., 142, 124 and 131 kJ/mol, respectively.34) On the other hand, since the specimens quenched from the solutionised temperature involve quite dense super-saturated quenched-in-vacancies, the activation energy will comprise mainly that of vacancy migration. In fact, the activation energies reported for vacancy migration in Al matrix are in the range from 0.4 to 0.75 eV,35) i.e., from 39 to 72 kJ/mol
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and are in keeping with the activation energy obtained in the present experiment. The exothermic heat due to the reaction A is in the ranges from 1.9 to 3.8 J/g as described above. If the reaction A arises from the annihilation of vacancies by both the collapse of vacancy clusters and the migration to various vacancy sinks, the heat will be in the range from 2.6 to 26 J/g corresponding to the densities of dissipated vacancies in the range from 0.01 to 0.1 mol. Of course, vacancies will not be fully dissipated and the formation energy of dislocation loops should also be taken in account, the latter being about 20% in the case of the loops of 10 nm in diameter. Considering these requirements, the heat obtained is in the reasonable range for the interpretation as the dissipation of vacancies by migrating to the sinks such as grain boundaries and forming dislocation loops. It should also be noted that the present DSC results do not eliminate the possibility of solute atom cluster formation because solute atom clusters are also formed by the vacancy migration. However, in order to explain the temperature separation between DSC-A and PH1 as well as TEM results, it will be reasonable to interpret the DSC-A as the annihilation of vacancies by forming prismatic dislocation loops and also migrating to the sinks such as grain boundaries.

The broad increase in hardness at temperatures 50–80 K above the reaction A (PH1), is probably due to the formation of solute atom clusters. Since the peak height in hardness increases with increasing excess Si content as can be seen in Fig. 1, it is likely that the solute atom clusters comprise mainly Si atoms. The possibility of Mg co-clustering, which was confirmed by Murayama and Hono by means of AP-FIM, of course, cannot be eliminated. The assumption that PH1 corresponds to the solute atom cluster formation is also supported by the properties of the endothermic reaction B. That is, if PH1 arises from the formation of solute atom clusters, the reaction B will be due to the dissolution of them. In fact, the absorbed heat for the reaction B increases with increasing excess Si content as shown in Fig. 2 but the activation energy for it is independent of the excess Si content, about 165 kJ/mol, and is rather close to those for solute atom diffusions, as can be seen in Fig. 4(b). This result suggests that the formation and dissolution of solute atom clusters occur in these processes.

Reaction C is associated with the precipitation of β″ needles as reported in various literatures. The enthalpy change of the reaction C increases from 5 to 10 J/g with increasing excess Si from −0.26 to 0.57 at%. These values are very close to those obtained previously in a 6061 alloy, i.e., from 4.83 to 6.81 J/g. The activation energies for these reactions, however, are in the range from 100.8 to 118.8 kJ/mol and are significantly smaller than those for the solute atom diffusion in Al matrix. This may be due to the interaction between the reactions C and D. If the reaction D starts before the reaction C completes, the higher temperature side of the reaction C will be replaced by the reaction D. Thus, the higher temperature side of the true peak C will be lost, consequently the apparent peak temperature being lowered. Since the reaction D at a slow heating rate starts prior to the completion of the reaction C much faster than that at a rapid heating rate, the apparent peak C in slow heating will displace to lower temperatures, resulting in the low activation energy as expected from the Kissinger equation. This may explain the low activation energy of this reaction.

On the other hand, the next reaction D has been interpreted as the growth process of β″ needles into β′′ rods so far. It should, however, be emphasised that most of such conclusions are based on the fact that β″ needles transform eventually into β′ rods during the isothermal ageing at temperatures lower than the reaction D peak in continuous heating. If this conclusion was true, the peak height ratio in Fig. 3, $h_D/h_C$, would have increased with increasing excess Si content because the amounts of rodlike precipitates increase with increasing excess Si content as described in a previous paper. However, $h_D/h_C$ decreases drastically with increasing excess Si content above 0.2%. It should also be noted that cuboid β′-Mg$_2$Si particles precipitate densely in the excess Al matrix. Thus, the reaction D arises probably from the precipitation of β′-Mg$_2$Si particles. Suzuki et al. however, confirmed by the in-situ TEM observation that cuboid β′ particles nucleate at β′ rods and grow with consuming the rods at temperatures from 481–523 K after the isothermal ageing at 523 K for 10 min. Unfortunately in their study the diffraction pattern showing that the rodlike precipitates were really of β′
phase were not shown. According to our unpublished work, many $\beta'$ needles were recognised in this ageing condition although the average size of them was much larger than those initially formed, the crystal structure and the $\beta'/\text{matrix}$ orientation relationship being in keep with those determined by Andersen. Thus, it can also be interpreted that cuboid $\beta$ particles nucleate at the interfaces of $\beta''$ needles. This interpretation is supported by the fact that the reaction D follows immediately after the reaction C. The reason that the formation of $\beta'$ rods did not produce a well defined peaks in DSC curves may arise from the small exothermic heat for their formation. Similar effects are also observed in the case of the precipitation of Type-B rods and Si particles.

In the continuously heated excess Mg specimens, rodlike precipitates could not be detected in all the temperature range examined. Matsuda et al., however, observed $\beta'$ rods forming in the excess Mg alloy aged isothermally at 473 K for long time. In the case of isothermal ageing at lower temperatures where the atomic diffusion is slow, the precipitates with the atomic structure similar to that of the matrix will preferentially form at least in the early stages of ageing. On the other hand, in the specimens continuously heated to higher temperatures, more stable phases will precipitate even if the structures of them are significantly different from that of the matrix. Thus, the precipitation sequence in continuous heating will largely deviate from that in isothermal ageing.

In the quasi-binary and the excess Si alloys aged to temperatures above 635 K at 50 K/min, rodlike precipitates are recognised. These rods in the quasi-binary alloy are $\beta'$ phase but in the excess Si alloys both $\beta'$ and Type-B rods form. Coarse Type-A rods have been observed in the excess Si alloys isothermally aged. In the present continuously heating experiments, however, both Type-A and -C rods could not be detected. This may also arise from the difference in the precipitation kinetics described above.

Although TEM results have not been shown at present, the final precipitation reaction E and the following large endothermic reaction F in Fig. 2 are the formation of stable $\beta$-Mg$_2$Si plates and the dissolution of them in the matrix, respectively, as reported in various literatures.

5. Conclusions

The precipitation behaviours during continuous heating in the Al–Mg–Si alloys with excess Mg and Si contents have been investigated by means of Vickers hardness measurements, DSC and TEM. The results obtained are as follows.

(1) The precipitation sequence during continuous heating may be summarised as: vacancy annihilation by both forming prismatic dislocation loops and migrating to various sinks $\rightarrow$ solute atom cluster formation $\rightarrow$ dissolution of solute atom clusters $\rightarrow$ needle-shaped $\beta''$ precipitation $\rightarrow$ precipitation of fine cuboid $\beta$-Mg$_2$Si particles $\rightarrow$ precipitation of $\beta''$ rods in the quasi-binary alloy (in the excess Si alloys, the precipitation of $\beta''$, Type-B rods Si particles $\rightarrow$ precipitation of $\beta$-Mg$_2$Si plates $\rightarrow$ dissolution of them into the matrix.

(2) The first exothermic reaction A occurring at the lowest temperatures arises probably from the vacancy annihilation by the collapse of vacancy clusters and the migration to sinks such as grain boundaries. The prismatic dislocation loops formed by the collapse of vacancy clusters are observed.

(3) The broad hardening (PH1) following the reaction A increases with increasing excess Si content. It is likely that this hardening is due to the formation of solute atom clusters.

(4) The sharp and large exothermic reaction C inducing large hardening corresponds to the precipitation of $\beta''$ needles. Increasing excess Si content accelerates this reaction.

(5) The reaction E arises probably from the precipitation of $\beta$-Mg$_2$Si particles. In the excess Mg and the quasi-binary alloys, cuboid particles showing $\beta$-Mg$_2$Si structure can be clearly observed at temperatures around this reaction but the increase of excess Si content results in the decrease of their density.

(6) In the quasi-binary alloy $\beta'$ rods precipitate following the formation of cuboid $\beta$ particles, but in the excess Si alloys both $\beta'$ and Type-B rods form.

Acknowledgements

Y. O. and K. N. would like to express sincere thanks to the Ministry of Education and Science for providing the Research Grant-in-Aids for the promotion of this research. L. C. D. would like to thank The Rotary Club for providing the scholarship for this research.

REFERENCES

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