Morphology and thermal stability of metastable precipitates formed in an Al-Mg-Si ternary alloy aged at 403 K to 483 K

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Abstract

Morphology and thermal stability of metastable phase precipitates formed in a balanced (Mg/Si=2) Al-Mg-Si alloy were studied by means of high-resolution electron microscopy (HRTEM) observations and differential scanning calorimetry (DSC) measurements. The present study revealed that the four types of precipitate morphology were found in the HRTEM images, that the heat change of the exothermic peak P in DSC measurements was mainly caused by the formation of type-2 and 3 precipitates in morphology and that the heat change of the exothermic peak Q which was yielded after the peak P probably corresponded to the formation of type-4 precipitates .

Keywords: Heat treatment; Electron microscopy; Microstructure; Al-Mg-Si alloy; Differential scanning calorimetry; Morphology of precipitates

1. Introduction

Aluminium-based Al-Mg-Si ternary alloys are widely used for practical applications, such as structural materials for transportation vehicles, vessels and construction. The precipitation behaviour in an Al-Mg-Si alloy has been generally considered to follow the sequence: supersaturated solid solution clusters metastable β'' metastable β' stable β [1-4]. Some papers have claimed that other metastable phases are additionally formed during isothermal ageing [5-9]. There are, however, a number of ambiguities in the

structure, alloy composition, and properties of metastable phases.

Differential scanning calorimetry (DSC) measurements and high-resolution transmission electron microscopy (HRTEM) observations are very helpful tools to investigate the precipitation behaviour in an Al-Mg-Si alloy, but there are few works which aim at quantitatively examining the relation between the thermal stabilities of phases detected by DSC measurements and the microstructures observed by HRTEM. This work was intended to clarify the precipitation behaviour and the thermal stabilities of the phases formed during isothermal ageing in an Al-Mg-Si alloy, using HRTEM observations and DSC measurements.

2. Experimental

Two Al-Mg-Si alloy specimens with balance compositions (Mg/Si=2 in atomic ratio) were used in this study. The chemical compositions of the alloy are listed in Table 1.

Table 1. Composition (at%) of the specimen studied

Alloy	Mg	Si	Al	Mg ₂ Si
B1	1.15	0.58	bal.	1.59
B2	0.75	0.41	bal.	1.12

The 75mm-diameter billets were extruded at 773 K and the sheets were formed by cold rolling. The final test specimens were solution-treated at 828 K for 3.6 ks and subsequently quenched in ice water. Then they were isothermally aged in an oil-bath at 403 K from 0.06 ks to 4800 ks, at 433 K from 0.06 ks to 900 ks, at 463 K from 0.06 ks to 600 ks, and at 483 K from 0.06 ks to 60 ks. The ageing time was chosen from an early stage to overage, to consider the wide range of precipitation process at these temperatures. A Topcon EM-002B microscope was used at 180 kV accelerating voltage. HRTEM images were taken along the crystallographic 001 orientation in the Al matrices. Nine reflections

— the transmitted beam, four 200 and four 220 reflections symmetrically excited — were used to obtain the HRTEM images. The DSC measurements were conducted using a Rigaku TAS300-8230D instrument with a heating rate of 0.17 K/s.

3. Results and discussion

3.1. Morphology and the density of the precipitates

Fig. 1 shows a typical HRTEM image of the precipitates for the B2 specimen aged at 433 K for 60 ks. The precipitate indicated by arrow (a) shows an irregular arrangement of black-white contrast inside the precipitate. However, two other precipitates are simultaneously observed with parallelogram lattice fringes, as indicated by arrows (b) and (c).

Fig. 1. HRTEM images of the precipitates for the B2 specimen aged at 433 K for 60 ks

Careful HRTEM observations of the B1 and B2 specimens, which were aged for up to 7200 ks at four different ageing temperatures from 403 K to 483 K, revealed that the

morphology of precipitates could be classified as four types, as shown in Fig. 2. Based on the HRTEM observations, we specified the following four types of precipitates. The type-1 precipitate is approximately 1 to 2 nm in size and shows a very weak contrast inside the precipitate. Type-2 is slightly larger, 3 to 8 nm in size, and ellipsoidal in shape with an irregular arrangement of black-white contrast internally. The type-3 precipitate shows a parallelogram-shaped image that is 3 to 8 nm in size, and has lattice fringes mutually intersecting at an angle of 65° to 80° . Type-4 is an ellipsoidal precipitate 6 to 11 nm in size, which is approximately twice as large as the type-3 precipitate. This type of precipitate has apparently similar contrast to the type-3 precipitate, but the lattice fringes intersect at an angle of 60° .

We first considered the change in density of each type of precipitate versus ageing time. Fig. 3 (a), (b), (c) and (d) show the changes in the density of the precipitates of type-1, type-2, type-3 and type-4, respectively. The foil thickness was not precisely measured, but was estimated to be approximately 40 nm, referring to the data obtained by electron energy loss spectroscopy (EELS). In all cases, the peak position moved toward shorter times when the ageing temperatures increased. The type-1 precipitate density decreased as the ageing temperature decreased. The density curve for type-2 increased at lower temperatures and took a very high value at 403 K. The curve for type-3 is comparable to type-1 in height at 463 K and appeared later than type-1. The density of type-3 did not increase continuously, but saturated at 463 K. Although type-4 precipitates were observed at 483 K and 433 K, the density of these precipitates was relatively small.

Fig. 2. Four types of precipitate morphology on the HRTEM images

Fig.3. Changes in the density of the precipitates of each type with ageing time for B2, (a) Type-1, (b) Type-2, (c) Type-3 and (d) Type-4

3.2. Thermal stability

Fig. 4 shows the DSC curves for B2 specimens that were as-quenched and aged at 403 K. The curve for the as-quenched specimen has four large exothermic peaks at approximately 350 K (peak K), 550 K (peak P), 580 K (peak Q) and 730 K (peak S), respectively. We attributed peak K to the formation of solute clusters, peaks P and Q to two metastable phases, and peak S to the stable phase β_2 , through reference to [4, 5, 8].

The area of peak P decreases with the ageing time of isothermal annealing. Measuring the reduction of the peak area, we defined the difference of heat as $h(P) = h_{AsQ}(P) - h(P)$ and $h(Q) = h_{AsQ}(Q) - h(Q)$, where $h_{AsQ}(P)$, $h_{AsQ}(Q)$, $h(P)$, and $h(Q)$ are the heat for peak P

and peak Q of the as-quenched and aged specimens, respectively. The difference in heat corresponds to the amount of the precipitates in the isothermal ageing [10,11]. Fig. 5 (a) shows the quantity; $h(P) = h(P)_{AsQ} - h(P)$ in case of peak P, which corresponds to the amount of the precipitates in the case of $h(P) = 0$. The heat; $h(P)$ appearing after isothermal annealing apparently shows the residue of the precipitation occurring during isothermal annealing. The heat; $h(P)$, however, resulted from the balance of the residual precipitation $h(P)_1$ and the reversion $h(P)_2$ in the DSC measurement. Following the above consideration, the negative balance possibly arose from the fact that the precipitation in the isothermal annealing was comparatively large and the reversion $h(P)_2$ surpassed the residual heat $h(P)_1$, as shown in Fig. 5 (b).

Fig. 5. The heat corresponding to precipitates amount formed during isothermal annealing ; $h(P)$

Fig.6 shows the difference in heat obtained from the DSC curves shown in Fig. 4. The heat for peaks P and Q, which are partly superimposed on each other, were separated using commercial GRAMS/32 arithmetic computer software. The difference in heat $h(P)$ exhibits an S-shape curve with respect to ageing time at each temperature, and the curve reaches a saturated level at a certain ageing time as shown in Fig. 6(a). The plateau of $h(P)$ gradually moved toward longer ageing times and its value increased at lower ageing temperatures. Fig. 6(b) shows, however, that little change in $h(Q)$ occurred with respect to the ageing temperature and a small change within the range of approximately 5 Jg^{-1} was seen across the ageing period. Comparing the results shown in Fig. 3 and Fig. 6, the features of the heat difference suggest that $h(P)$ is closely related to type-2, and $h(Q)$

to type-4.

Fig. 6. (a) Relationship between $\Delta h(P)$ and ageing time, (b) Relationship between $\Delta h(Q)$ and ageing time

We examined the quantitative relationship between the heat $\Delta h(P)$ and $\Delta h(Q)$ and the density of each type of precipitate. Fig. 7(a) shows the relationship between the density of each type of precipitate and the heat difference $\Delta h(P)$ for the B2 specimens aged at 403 K to 483 K. Fig. 7(b) and (c) show the relationship between the density of each type of precipitate and $\Delta h(P)$ and $\Delta h(Q)$ for the B1 specimen aged at 483 K, respectively. Strong correlations between the density of the precipitates and the difference in heat are clearly apparent in Fig. 7(a) to (c). In the present analysis, the correlation coefficients between $\Delta h(P)$ and type-1, type-2, type-3, type-4, and type-2+3 were estimated at -0.64 ,

0.90, 0.40, -0.03, and 0.93, respectively, for the B2 specimens. The high correlation coefficient (0.93) obtained between $h(P)$ and the density of the type-2+3 precipitates for the B2 specimens and the high correlation coefficient (0.99) for the B1 specimen are of special interest. Fig. 7(c) shows that $h(Q)$ had a high correlation coefficient (0.82)

Fig. 7. Correlation between the density of each type of precipitate and (a) $h(P)$ for B2, (b) $h(P)$ for B1 and (c) $h(Q)$ for B1.

with the density of type-4 for the B1 specimen. Thus, the present quantitative analysis strongly suggests that the change of peak P in the DSC curve is mainly caused by the

formation of type-2 and 3 precipitates, and that the change of peak Q is caused by the formation of the type-4 precipitate .

4. Conclusions

The four types of precipitate morphology were found in the HRTEM images of the Al-Mg-Si alloy with two balance compositions. With respect to the relationship between the change of the peak in the DSC measurements and the density of the precipitates, we also conclude that the change in peak P is mainly caused by the formation of type-2 and 3 precipitates. The change of the exothermic peak Q, which is yielded after the peak P in DSC measurements, probably corresponds to the formation of type-4 precipitates .

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Figure captions

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