Effects of Natural Aging on Bake Hardening Behavior of Al–Mg–Si Alloys with Multi-Step Aging Process

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In the present paper, the effects of natural aging on the bake hardening behavior of four Al–Mg–Si alloys, i.e., Alloy A (Al–0.6Mg–0.6Si) (mass%), Alloy B (Al–0.6Mg–1.0Si), Alloy C (Al–1.0Mg–0.6Si) and Alloy D (Al–1.0Mg–1.0Si), were investigated by means of Vickers hardness test, tensile test, differential scanning calorimetry analysis (DSC) and transmission electron microscopy (TEM). Two kinds of nanoclusters, i.e., Cluster(1) and Cluster(2), were controlled with the multi-step aging process. As the results, it was found that Cluster(1) formed during natural aging caused the decreased bake hardening response even though the pre-aging was conducted before natural aging. The decrease of the bake hardening response with increasing the natural aging time was markedly higher in the later stage of bake hardening than in the early stage. Exothermic peaks of Peak 2 and Peak 2′ were observed in all of four alloys pre-aged at 343 and 363 K. Peak 2′ became larger with the natural aging time. The size distribution of the β precipitates became wider with the natural aging time for Alloy A heated up to the temperature of Peak 2. This is well understood by the following model. The transition from Cluster(2) formed during pre-aging to β precipitates occurs preferentially at the early stage of bake hardening or during heating up to the temperature of Peak 2. Then the growth of β precipitates is inhibited by the presence of Cluster(1) at the later stage of bake hardening. The secondary nucleation of β precipitates occurs after the dissolution of Cluster(1) into the matrix during heating up to the temperature of Peak 2. The combined formation of Cluster(1) and Cluster(2) by the multi-step aging essentially affects the BH response and the β precipitates in Al–Mg–Si alloys. [doi:10.2320/matertrans.L-M2014827]

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1. Introduction

Recently, Al–Mg–Si alloy sheets are widely used for automotive body panels in order to reduce the automotive body weight and thus to improve fuel efficiency in the cars. Al–Mg–Si alloys are selected for these applications because of their good performance of formability, corrosion resistance, surface quality and precipitation hardening during the paint-baking process, typically at 443–458 K (i.e., bake-hardening, BH). In the Al–Mg–Si based alloys, it is well known that the so-called “negative effect of two step aging” occurs, which is the significant decrease of the bake hardening response during the storage at room temperature before the bake hardening treatment. It is understood that the clustering of solute atoms (or some pre-precipitates) during the first step aging affects the formation of the strengthening β precipitates in the final aging.1–5) Yamada et al.5) reported based on the calorimetry analyses that two types of nanoclusters of solute atoms are formed, one is formed at lower temperatures up to 343 K and another is formed at higher temperatures than 343 K. Serizawa et al.5) clarified the characteristics of the both types of nanoclusters, Cluster(1) and Cluster(2), using a three dimensional atom probe technique (3DAP). They found that Cluster(1) formed at room temperature is stable at the BH temperature, whereas Cluster(2) formed at 373 K enhances the formation of the β phase.

On the other hand, the pre-aging process was proposed to prevent the “negative effect” in the industrial production process. In this process, Al–Mg–Si alloys are heat-treated with the multi-step aging process such as the sequence of pre-aging, natural aging and final aging (bake hardening). In the multi-step aging, Kim et al.6) reported that the formation of Cluster(1) during natural aging is effectively suppressed by Cluster(2) formed by pre-aging. However, in these previous work6,7) on the multi-step aging process, the natural aging times was considered to be not enough to clear the role of natural aging. The present authors8) reported that the alloys pre-aged at 343–383 K showed natural age hardening during the sufficiently long term exposure at room temperature and resultanty the bake hardening response decreased with increasing natural age hardening. In the previous report, the results revealed that Cluster(1) formed during natural aging caused the decreased bake hardening response even though the pre-aging was conducted before natural aging. However, in the multi-step aging process, the clustering behavior with natural aging time and especially the effect of clusters on the formation of the β phase during final bake hardening are still unclear. Furthermore, almost all the previous researches on the multi-step aging process of Al–Mg–Si alloys were performed using only one alloy composition, although the alloy composition will affect the clustering and bake hardening behaviors. Then, the aim of this study is to investigate the role of prolonged natural aging on the formation of the β precipitates during final bake hardening in the multi-step aging process. Four kinds of alloys containing different amount of Mg and Si corresponding to AA6022, AA6014 and AA6182 alloys were used. These are typical alloys used for the automotive body panels.

2. Experimental Procedure

The chemical compositions of the alloys used in this work...
are listed in Table 1. The amounts of Mg and Si in Alloy A, Alloy B and Alloy D correspond to AA6014, AA6022 and AA6182 alloys, respectively. Alloy C is a quasi-binary Al-Mg2Si alloy. The alloy ingots were homogenized at 833 K, hot-rolled and cold-rolled to sheets with the final thickness of 1.0 mm. The alloy sheets were solution heat treated at 843 K for 1.8 ks in a salt bath and quenched into the room temperature water, then, immediately pre-aged at 343, 363 and 383 K for 18 ks in a hot water bath or in an oil bath. No pre-aged samples were also prepared for comparison. The final bake-hardening treatment (artificial aging) was conducted at 443 K for 0.6-3.6 ks after natural aging for up to 4.5 \times 10^4 ks (about 1.5 years). The Vickers hardness was measured by AVK-C2 (Akashi) with 49 N load and a dwelling time of 15 s. 3. Results

3.1 Natural age-hardening and bake-hardening response

The hardness changes during natural aging are shown in Fig. 2(a) for Alloy A pre-aged at 343, 363 and 383 K and no pre-aged conditions. In all of the pre-aged specimens, hardness is not changed at the early stage of natural aging (up to \(1 \times 10^2\) ks) unlike in the no pre-aged specimen. However, the hardness of the pre-aged specimen increases after longer natural aging time. The increments of hardness comparing to the hardness measurement of samples after shortest aging (HV0); \(\Delta HV_{NA} = HV - HV_0\) are plotted in Fig. 2(b). The time to start increasing of the hardness becomes longer with increasing the pre-aging temperature. The time to start the hardness increase of \(\Delta HV\) for the specimens pre-aged at 343, 363 and 383 K are about \(2.5 \times 10^2\), \(1.5 \times 10^3\) and \(1 \times 10^4\) ks respectively. Whereas Fig. 2 have been reported previously, these are also shown in this paper to exhibit the relationship between the natural age hardening and the natural aging time when the DSC measurement in this study. The DSC

![Fig. 1](image1.png)

![Fig. 2](image2.png)

Table 1 Chemical compositions of the alloy specimens.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Al</th>
<th>Mg2Si</th>
<th>ex. Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.62 mass%</td>
<td>0.62 mol%</td>
<td>0.08 Bal.</td>
<td>Bal.</td>
<td>1.15 Mg/Si</td>
<td>1.03 Mg2Si</td>
</tr>
<tr>
<td>B</td>
<td>0.62 mass%</td>
<td>0.69 mol%</td>
<td>0.04 Bal.</td>
<td>Bal.</td>
<td>0.78 Mg/Si</td>
<td>0.55 Mg2Si</td>
</tr>
<tr>
<td>C</td>
<td>1.06 mass%</td>
<td>1.19 mol%</td>
<td>0.09 Bal.</td>
<td>Bal.</td>
<td>2.09 Mg/Si</td>
<td>0.03 Mg2Si</td>
</tr>
<tr>
<td>D</td>
<td>1.20 mass%</td>
<td>1.30 mol%</td>
<td>0.04 Bal.</td>
<td>Bal.</td>
<td>0.78 Mg/Si</td>
<td>0.25 Mg2Si</td>
</tr>
</tbody>
</table>

![Solution heat treatment](image3.png)

![Pre-aging](image4.png)

![Natural aging](image5.png)

![Bake hardening](image6.png)

![Artificial aging](image7.png)

![Heat treatment flow](image8.png)

![DSC measurement](image9.png)

![Hardness changes](image10.png)

![Vickers hardness](image11.png)

![Changes of hardness](image12.png)
measurement was performed at the natural aging time indicated by arrows in Fig. 2(b) in order to investigate the clustering behavior during natural aging.

The bake hardening response evaluated by the 0.2\% proof stress change during the final artificial aging is shown for Alloy A in Fig. 3. The specimens were pre-aged at (a) 343 K, (b) 363 K, (c) 383 K and (d) no pre-aging, subsequently, the bake hardening response decreased with the increase of the pre-aging temperature. In all alloys, the decreases of \( \Delta \sigma_{BH} \) is larger when pre-aged at 343 K than at 363 K. In the case of pre-aging at 343 K, the decreases of the proof stress at both of the early and later parts are larger, whereas at 363 K the decreases at the early and later parts are negligible and small.

Assuming that the early part of the bake hardening is due to the formation of the \( \beta'' \) phase and the later part is due to the growth of the \( \beta'' \) phase, it is considered that the growth of the \( \beta'' \) phase is suppressed by Cluster(1) formed during natural aging in the alloys pre-aged at 363 K. The formation of the \( \beta'' \) phase is also suppressed by Cluster(1) in the alloys pre-aged at 343 K, especially in Alloy B and Alloy D.

3.2 DSC analysis for the natural aging and the \( \beta'' \) phase formation

Figure 5 shows the DSC curves for the Alloy A naturally aged for various times after pre-aging at 343 K, while partial DSC curves have previously reported. Each of the DSC curves corresponds to the natural aging time indicated by an arrow in Fig. 2. No endothermic peak of Peak 1 is detected at around 495 K for the alloys naturally aged for 86.4 and 259 ks. Peak 1 is observed when naturally aged for longer time than 605 ks and becomes larger with the natural aging time. According to the previous work, this endothermic peak is due to the dissolution of clusters formed during natural aging. Therefore, the obtained results indicate that Cluster(1) is newly formed during natural aging, and the amount of Cluster(1) increases with the natural aging time.

In the DSC curves, the exothermic peaks of Peak 2 and Peak 2' at around 525 and 540 K are observed in same time, whereas the present authors have reported that the Peak 2 shifts to Peak 2' with natural aging time from the comparison between the DSC curves for Alloy A naturally aged for 86.4 and 5.77 \( \times 10^5 \) ks after pre-aging at 343 K. Only Peak 2 is observed when naturally aged for 86.4 ks. Peak 2 is also still
observed when naturally aged for longer time than 259 ks. Peak 2′ becomes larger with the natural aging time and finally becomes only one peak in the DSC curve for the natural aging for 5.77 × 10^3 ks. Peak 2, however, still remains as a shoulder in the DSC curves naturally aged for 1.04 × 10^4 and 4.48 × 10^4 ks. Both of Peak 2 and Peak 2′ are due to the formation of β″ [2,10], therefore it is understood that the formation of the β″ phase occurs in the two stages in these conditions. The formation behavior of the β″ phase must be affected by the natural aging.

Figure 6 shows the DSC curves for the Alloy B at various natural aging times after pre-aging at (a) 343 K and (b) 363 K. In the DSC curves for Alloy B pre-aged at 363 K, both of Peak 2 and Peak 2′ are observed through the natural aging for 86.4 to 1.04 × 10^4 ks. Peak 2′ becomes larger with the natural aging time and subsequently only one peak at 4.48 × 10^4 ks, whereas the size of Peak 2 is almost constant. In this case, the endothermic Peak 1 is observed at all of the natural aging time. Only Peak 2 is observed, in contrast, for the aging time of 86.4 to 1.04 × 10^4 ks for Alloy B pre-aged at 343 K, then both of Peak 2 and Peak 2′ are observed at the natural aging time of 4.48 × 10^4 ks. The temperatures for Peak 2 and Peak 2′ determined in the all DSC curves are plotted with the natural aging time in Fig. 7. Both of Peak 2 and Peak 2′ are observed in many cases for each alloy, these separated two peaks are found to be common in the multi-step aging of the pre-aging and natural aging process. Peak temperatures are almost unchanged or slightly increase with the natural aging time. Then, the peak temperatures are considered to be independent on the pre-aging temperature in each alloy. This indicates that the formation temperature of β″ is not changed even if the amount of Cluster(2) is changed. In Figs. 7(b) and 7(d), only Peak 2 is observed until the natural aging time of 1.04 × 10^4 ks for Alloy B and Alloy D pre-aged at 343 K.
aged at 343 K. The increase of the temperature of Peak 2 with the natural aging time for the both alloys pre-aged at 343 K is larger than that for other conditions. These results show that Cluster(1) formed during natural aging inhibits the formation of $\beta''$ more effectively in these conditions.

3.3 TEM observation of precipitates

In order to identify the precipitation behavior corresponding to the separated exothermic peaks in the DSC curves, TEM observation was performed using the samples with the same heat flow as the DSC measurement. The specimens of Alloy A pre-aged at 343 K were heated up to 523 and 543 K corresponding to Peak 2 and Peak 2$'$ respectively, then quenched into water. The heating rate was 0.167 K/s (10 K/min), exactly the same as DSC. This heat treatment was conducted for the specimens naturally aged for 86.4, 673 and $1.26 \times 10^3$ ks.

The TEM observation results are shown in Fig. 8. As indicated in Fig. 8 for the specimen heated up to 523 K, the size and number density of the $\beta''$ precipitates are reduced with increasing the natural aging time. On the contrary, after heating up to 543 K, the number density of the $\beta''$ precipitates is also reduced but their size is increased with increasing the natural aging time. During heating from 523 to 543 K, some of the $\beta''$ precipitates are coarsened rapidly in the specimens naturally aged for 673 and $1.26 \times 10^3$ ks than that in the specimen naturally aged for 86.4 ks. In the enlarged TEM micrograph of Fig. 8(f) for the alloy heated up to 543 K after naturally aged for $1.26 \times 10^3$ ks, some very small precipitates are clearly observed as indicated by arrows in the enlarged micrograph in Fig. 9, whereas some neighbor precipitates are already markedly coarsened. These small precipitates are considered to be nucleated later than the coarsened precipitates. The size distributions of precipitates are measured from the TEM micrographs for the specimens heated up to 543 K. In this study, only the length of needle shaped precipitates was measured as the precipitate size. The results are shown in Fig. 10. According to the increasing the natural aging time, the frequency of the larger size
Fig. 7 Changes of peak temperatures of Peak 2 and Peak 2’ during the natural aging time in all DSC curves in this study. (a) Alloy A, (b) Alloy B, (c) Alloy C, and (d) Alloy D.

Fig. 8 TEM bright field images of the Alloy A pre-aged at 343 K after heating up to 523 and 543 K, then quenched into water. Heating rate: 0.167 K/s (10 K/min). The heat treatment was conducted for the specimens naturally aged for 86.4, 673 and 1.26 x 103 ks.
precipitates than 40 nm increases and the peak frequency decreases. Therefore, the size distribution of $\beta''$ becomes wider with the natural aging time.

The number density of smaller precipitates than 10 nm in the alloy naturally aged for 673 ks becomes higher than that in the alloy naturally aged for 86.4 ks. These results suggest that the $\beta''$ formation occurs in the two stages during heating, one is at around 523 K and another is at around 543 K for the Alloy A naturally aged for 673 and $1.26 \times 10^3$ ks. After natural aging for 86.4 ks, in contrast, the $\beta''$ precipitates are formed mainly at one time at around 523 K, then grow normally during heating up to 543 K.

4. Discussion

All of the pre-aged alloys exhibited the higher bake hardening response than the no pre-aged alloys in this study. The bake hardening response of the pre-aged and subsequently naturally aged alloys decreased with increasing the natural aging time. The DSC results indicate that the decrease of the bake hardening response (the negative effect) is caused by Cluster(1) formed during natural aging.

In many cases, when natural age hardening and the resulted decrease of the bake hardening response occur, the separated exothermic peaks were detected in the DSC curves. Figure 11 shows the results of DSC for Alloy B pre-aged at 363 K and then naturally aged for 1.23 $\times 10^3$ ks (PANA), exhibiting two separated peaks, Peak 2 and Peak 2'. The results of DSC for Alloy B only pre-aged at 363 K (PA) and only naturally aged for $1.2 \times 10^3$ ks (NA) are also shown in the figure.

The number density of smaller precipitates than 10 nm in the alloy naturally aged for 673 ks becomes higher than that in the alloy naturally aged for 86.4 ks. These results suggest that the $\beta''$ formation occurs in the two stages during heating, one is at around 523 K and another is at around 543 K for the Alloy A naturally aged for 673 and $1.26 \times 10^3$ ks. After natural aging for 86.4 ks, in contrast, the $\beta''$ precipitates are formed mainly at one time at around 523 K, then grow normally during heating up to 543 K.
aging time as shown in Fig. 4 and also the results of TEM observation as shown in Figs. 8, 9 and 10. The \( \Delta P_{BH} \) in the later stage of the bake hardening decreases with the natural aging more effectively than that in the early stage. It is supposed that the transition from Cluster(2) to \( \beta'' \) occurs in the same manner as only Cluster(2) exists in the early stage of the bake hardening even Cluster(1) coexists, but Cluster(1) suppresses the growth of \( \beta'' \) in the later stage with the amount of itself. The two stage formation of \( \beta'' \) suggested from the TEM observation is considered to be corresponding to the transition from Cluster(2) to \( \beta'' \) and the nucleation of \( \beta'' \) after the dissolution of Cluster(1), respectively.

Figure 12 shows the schematic illustration for the structure transition model assumed in this study during the heat treatment with the same conditions as DSC. When Cluster(2) is only formed, \( \beta'' \) is transformed and grow as described in the previous work.\(^4\)\(^6\) When Cluster(1) and Cluster(2) coexist, \( \beta'' \) is transformed from Cluster(2) during heating up to Peak 2, but the growth of \( \beta'' \) or further nucleation in the matrix is suppressed. This suggests that Cluster(1) still partially remains and prevents the formation of \( \beta'' \) until the temperature for Peak 2 which is higher than that of the endothermic Peak 1 due to the dissolution of Cluster(1). Then, Cluster(1) is dissolved and provides solutes and vacancies, these effectively enhance rapid coarsening and secondary nucleation of \( \beta'' \) when it is heated up to Peak 2'. The above proposed model to explain the separated two peaks in the DSC curves will be experimentally confirmed, for example, by the HRTEM observation. Matsuda et al.\(^1\) reported the HRTEM images of several types of precipitates formed correspondingly to the DSC curves.

Comparison among the alloys in this study, the decrease of \( \Delta P_{BH} \) with the natural aging time in the early stage of the bake hardening is largest for Alloy B and Alloy D pre-aged at 343 K. In these conditions, the increase of the Peak 2 temperature with the natural aging time is higher than that in other conditions. The endothermic peak areas of Peak 1 for Alloy B when naturally aged for longer time than \( 1.21 \times 10^3 \) ks are larger compared with that for Alloy A as shown in Figs. 5 and 6. The peak area of Peak 1 for Alloy D is also larger than Alloy A and Alloy C. Therefore, it is found that in these conditions the amount of Cluster(1) formed during natural aging is higher than that in other conditions and therefore the increased amount of Cluster(1) suppresses more strongly the formation of \( \beta'' \) through Cluster(2).

5. Conclusions

The bake hardening behavior with multi-step aging in four kinds of A–Mg–Si alloys containing various amounts of Mg and Si was investigated. The results obtained in this study are summarized as follows.

(1) The bake hardening response decreases with the natural aging time. The decrease of the bake hardening response is markedly higher in the later stage of the bake hardening than that in the early stage. The changes of the bake hardening response in the early stage depend on the pre-aging temperature and the alloy composition.

(2) Two exothermic peaks, i.e., Peak 2 and Peak 2' in the DSC curves are found in all of four alloys pre-aged at 343 and 363 K. Peak 2' becomes larger with increasing the natural aging time. The size distribution of \( \beta'' \) for Alloy A heated up to the temperature of Peak 2' becomes wider with the natural aging time.

(3) The combined formation of Cluster(1) and Cluster(2) by the multi-step aging process causes the two stage formation of the \( \beta'' \) phase. One is the transition from Cluster(2) to the \( \beta'' \) phase and another is the nucleation of the \( \beta'' \) phase after dissolution of Cluster(1).
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