Combined Effect of Pre-Straining and Pre-Aging on Bake-Hardening Behavior of an Al-0.6 mass%Mg-1.0 mass%Si Alloy

Tetsuya Masuda1,2,*1, Yasuo Takaki2, Takeo Sakurai2,*2 and Shoichi Hirosawa1

1Department of Mechanical Engineering and Materials Science, Yokohama National University, Yokohama 240-8501, Japan
2Aluminum Sheets and Coils Research Department, Kobe Steel, Ltd., Moka 321-4367, Japan

The effect of pre-straining in combination with pre-aging on bake-hardening behavior of an Al-0.6 mass%Mg-1.0 mass%Si alloy was investigated by means of Vickers hardness test, electrical conductivity measurement, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Hardness change and DSC analysis revealed that only 3% pre-strain suppresses the formation of clusters; i.e. cluster(1), during single aging below 343 K. On the other hand, by combining with pre-aging at 343 K, pre-straining was found to improve bake-hardening response during final aging at 443 K. TEM observation confirmed that the improvement of bake-hardening response by pre-straining is mainly due to the enhanced precipitation of β′ phase in the matrix. These results are explained by the consideration that dislocations induced by pre-straining reduce the concentration of quenched-in excess vacancies, resulting in both the suppressed clustering of solute atoms during pre-aging and the accelerated precipitation of the β′ phase from more supersaturated solute atoms in final aging.

[doi:10.2320/matertrans.L-M2009831]

(Received July 15, 2009; Accepted November 4, 2009; Published January 25, 2010)

Keywords: aluminum-magnesium-silicon alloy, pre-straining, pre-aging, clusters, bake-hardening, two-step aging, dislocations, vacancy concentration

1. Introduction

Recently, aluminum alloys have come into use for automotive body panels in order to reduce weight and thus to improve fuel efficiency. Basic requirements for this application are not only to possess high formability, limited spring back and high hemming performance during forming process, but also to exhibit high strength after paint-bake treatment (e.g. at 443 K). This is often accomplished by controlling yield strength of the alloys, i.e. lower yield strength before forming process and higher yield strength after paint-bake treatment.

Heat treatable Al-Mg-Si alloys are mainly used for this application because of their good formability, corrosion resistance, surface quality and remarkable precipitation strengthening after paint-bake treatment. It is well known that the β′ phase greatly contributes to bake-hardening in this alloy system and the alloys containing excess of Si over Al-Mg2Si quasi-binary composition exhibit pronounced bake-hardening response.1–3) Previous work suggested that pre-aging conditions significantly affect the formation of clusters in the early stages of phase decomposition and bake-hardening behavior of these alloys.4–6) The author et al.7) reported that two types of clusters: i.e. cluster(1) and cluster(2), are formed competitively in this alloy system. Cluster(1), formed below ~343 K including room temperature, decreases the number density of the β′ phase and results in negative effect of two-step aging due to its high thermal stability even at paint bake temperatures. On the other hand, cluster(2), formed at higher temperatures (e.g. 373 K), enhances the formation of the β′ phase because of the continuous transformation into the β′ phase. In this paper, the clusters formed in various pre-aging conditions are referred as to cluster(1) or cluster(2), as previously proposed by the author et al.7)

Pre-straining is known to have a substantial effect on precipitation kinetics and processes. For Al-Mg-Si alloys, previous work revealed by DSC analysis that pre-straining accelerates precipitation because of decreased activation energy for the growth of precipitates.8,9) Matsuda et al.10) reported that 5% pre-strain following pre-aged at 423 K for 60 ks improves bake-hardening response in under-aged condition and results in higher peak hardness at 473 K for an Al-0.37 mass%Mg-0.62 mass%Si alloy. Furthermore, Birol et al.11,12) reported that pre-straining shortly after solution heat treatment suppresses clustering behavior at room temperature, but results in the enhanced formation of the β′ phase during aging at 453 K. These suggest that the combined effect of pre-straining and pre-aging is quite useful, but still have room for investigation under various combinations of the amount of pre-strain and pre-aging temperature.

In this paper, the effect of pre-straining by 0.5% and 3% in combination of pre-aging at 298–373 K on bake-hardening behavior of an Al-0.6 mass%Mg-1.0 mass%Si alloy was investigated in attempts to clarify the effectiveness of pre-straining and pre-aging and thus to improve bake-hardening response of the alloy.

2. Experimental

The chemical composition of the alloy utilized in this work is listed in Table 1. The alloy ingot was homogenized and hot- and cold-rolled through the standard manufacturing process to the final thickness of 1.0 mm. The square-cut specimens were solution heat-treated at 823 K for 60 s, and then water quenched. The average grain size of the specimens is approximately 40 μm, as measured by a cross sectional
method. Pre-straining was introduced with a tensile testing machine for the specimens with 50 mm gauge length, taken from rolled sheet in the transverse direction, by 0.5 or 3% shortly after water quenched. Some specimens were processed without pre-straining for comparison.

The specimens were subjected to isothermal aging at 298, 313, 343 and 373 K (i.e. single aging). The holding time at room temperature was 300 s between quenched and isothermally aged. During aging, the hardness was measured by a Vickers hardness tester with 19.6 N load and dwell time of 15 s. The electrical conductivity was measured by an eddy current tester. For some specimens, differential scanning calorimetry (DSC) analysis was carried out under a heating rate 0.17 K/s. To investigate bake-hardening response in two-step aging, furthermore, final aging at 443 K for up to 1.2 ks was conducted for the specimens subjected to pre-aging at 298–373 K for 7.2 or 778 ks. Flow charts of the two heat treatments are shown in Fig. 1. For some specimens, transmission electron microscopy (TEM) observation was performed under accelerating voltage of 200 kV.

3. Results

3.1 Effect of pre-straining on single aging behavior

The changes of hardness during single aging at 298–373 K for the specimens without pre-strain, with 0.5% and 3% pre-strain are shown in Fig. 2. At 298 and 313 K the hardness is monotonously increased and then saturated with higher values of hardness at 313 K than those at 298 K. At 343 and 373 K the changes of hardness exhibit a two-stage increase and the rapid increase in the second stage starts around $10^5$ s and $10^6$ s, respectively. Concerning the effect of pre-straining, furthermore, the hardness decreases with increasing the amount of pre-strain at all the investigated temperatures. Therefore, pre-straining was found to retard age hardening during single aging in this temperature range.
The changes of electrical conductivity during single aging are shown in Fig. 3 for the specimens without pre-strain, with 0.5% and 3% pre-strain. At 298 and 313 K electrical conductivity decreases with aging time, whereas electrical conductivity at 343 and 373 K slightly increases around $3 \times 10^3$ s, and then rapidly decreases. At all the investigated temperatures, the changes in electrical conductivity become smaller with increasing the amount of pre-strain, suggesting that phase decomposition is retarded by pre-straining. These results well agree with the changes of hardness in Fig. 2.

To clarify how much phase decomposition proceeds during single aging, DSC analysis was carried out for the specimens without pre-strain and with 3% pre-strain as shown in Fig. 4. Endothermic peak around 480 K (Peak 1) becomes smaller with increasing single aging temperature, whereas Peak 1 becomes larger with increasing pre-aging time at 298 and 313 K. As for the effect of 3% pre-strain, furthermore, the area of Peak 1 becomes much smaller than that in the specimen without pre-strain. These results suggest that the amount of clusters responsible for Peak 1, i.e. cluster(1) formed during single aging below 343 K, becomes less with increasing not only pre-aging temperature but also the amount of pre-strain. In contrast, exothermic peak around 510 K (Peak 2) shifts to lower temperature by 3% pre-strain, irrespective of pre-aging conditions.
3.2 Effect of pre-straining on final aging behavior

The changes of hardness during final aging at 443 K are shown in Fig. 5 for the specimens without pre-strain, with 0.5% and 3% pre-strain, subjected to pre-aging at 298–373 K for 7.2 or 772 ks, or without pre-aging.

![Graphs showing changes of hardness during final aging at 443 K for different pre-aging conditions.](image)

Fig. 5 Changes of hardness during final aging at 443 K for the specimens without pre-strain, with 0.5% and 3% pre-strain, subjected to pre-aging at 298–373 K for 7.2 or 772 ks, or without pre-aging.

As for the effect of 0.5% and 3% pre-strain, furthermore, more enhanced hardness changes than the specimens without pre-strain are obtained when pre-aged at 298, 313 and 343 K (Fig. 5(a)–(c)). Note that pre-straining by 3% combined with pre-ageing at 343 K for 7.2 ks is most effective to improve bake-hardening response (Fig. 5(c)). The changes of electrical conductivity during final aging at 443 K are shown in Fig. 6 for the specimens without
pre-strain, with 0.5% and 3% pre-strain. The electrical conductivity of the specimens pre-aged at 298–343 K for 7.2 ks increases with aging time at 443 K, and becomes higher with increasing the amount of pre-strain (Fig. 6(a)–(c)). In particular, the change of electrical conductivity of the specimen with 3% pre-strain and pre-aged at 343 K exceeds that of the specimen without pre-aging (Fig. 6(g)) in good agreement with the change of hardness in Fig. 5. Therefore, it is confirmed that bake-hardening response at 443 K is enhanced through the accelerated phase transformation by virtue of the effectiveness of combined pre-straining and pre-aging.

Fig. 6 Changes of electrical conductivity during final aging at 443 K for the specimens without pre-strain, with 0.5% and 3% pre-strain, subjected to pre-aging at 298–373 K for 7.2 or 772 ks, or without pre-aging.
Figure 7 shows TEM bright-field and dark-field images together with selected area diffraction patterns (SADPs) of the specimens without pre-strain, with 0.5% and 3% pre-strain, subjected to pre-aging at 343 K for 7.2 ks and final aging at 443 K for 3.6 ks. These microstructures are responsible for the increase of hardness in the two-step aged specimens (Fig. 5(c)). Lower magnification images reveal that dislocation density becomes higher with increasing the amount of pre-strain. However, it is found from the dark-field image that some precipitates nucleate on dislocation lines (as indicated by arrows), but the amount is much less than those nucleating in the matrix because of the relatively small amount of pre-strain. The sphere- or needle-like precipitates in the higher magnification images are identified to the \( \text{C12}_0 \) phase from the streaks along \([100]_{\text{Al}}\) and \([010]_{\text{Al}}\) in SADPs, and enhanced by pre-straining, as suggested by stronger strain contrast for the specimens with 0.5% and 3% pre-strain. Therefore, it is confirmed that the improvement of bake-hardening response by pre-straining is mainly due to enhanced precipitation of the \( \beta' \) phase in the matrix.

4. Discussion

4.1 Suppressed formation of cluster(1) by pre-straining

The author et al. reported through 3DAP investigation that the hardness change during natural aging is associated with the formation of cluster(1) for an Al-0.95 mass%Mg-0.81 mass%Si alloy. It is believed that the type of clusters formed during single-aging in this work is the same as that in the previous work, since the alloy compositions utilized in both work locate in the same area showing similar age hardening behavior, i.e. negative effect of natural aging on bake hardening response.\(^{11}\) As shown in Figs. 2 and 3, the changes of hardness and electrical conductivity during single aging become lower with increasing the amount of pre-strain. Therefore, pre-straining prior to single aging suppresses the clustering of solute atoms, thus the formation of cluster(1), during single aging. This can be also confirmed by DSC traces (Fig. 4), where endothermic Peak 1, attributed to the dissolution of cluster(1), becomes smaller with pre-straining. Figure 8 compares heat of reaction for Peak 1, \( \Delta H_{\text{Peak1}} \), estimated by integrating a DSC trace under the baseline (Fig. 4) for the specimens single-aged at 298–373 K for 7.2 or 778 ks. \( \Delta H_{\text{Peak1}} \) of the specimens aged for 7.2 ks decreases with increasing aging temperature, and no endothermic peak is observed for the specimen aged at 373 K. As for the specimens aged for 778 ks, \( \Delta H_{\text{Peak1}} \) becomes larger than that in the specimens aged for 7.2 ks, suggesting that the amount of cluster(1) formed at 298 and 313 K increases with increasing aging time. Furthermore, it was also found in Fig. 8 that 3% pre-strain reduces \( \Delta H_{\text{Peak1}} \) below 343 K, confirming that pre-straining suppresses the formation of cluster(1) during aging at 298 and 313 K. Remember that the reason why the contribution of pre-straining is negligible in
the specimen pre-aged at 373 K is no formation of cluster(1), but cluster(2).

The clustering behavior of solute atoms in the earlier stage of phase decomposition strongly depends on vacancy concentration in alloys, and it is believed that dislocations induced by pre-straining act as sink sites for quenched-in excess vacancies. In general, dislocation density of well-aged specimens is thought to be \( N = 9.996\% \). Under the assumption that the above constants are related to true strain \( \varepsilon \) and evolution of resistivity per dislocation density \( \Delta \rho \):

\[
\Delta N = e^\varepsilon / \Delta \rho
\]

where \( A = 0.185 n \), \( n = 0.648 \) for an Al-0.47 mass\%Mg alloy and \( \Delta \rho = 3 \times 10^{-25} \Omega m^3 \) for high purity aluminum 99.996\%. Under this assumption, the above constants can be applied to the alloy utilized in this work, dislocation density of the specimen with 3\% pre-strain (i.e. \( \varepsilon = 0.0296 \)) \( N_{\text{pre-strain}} \) estimated as \( \sim 1 \times 10^{14} \) m\(^{-2} \) because \( \Delta N \) is much larger than \( N_{\text{annealed}} \). Furthermore, the average displacements between dislocations \( L \) are \( 1 \times 10^{-6} \)– \( 3 \times 10^{-6} \) m for the specimen without pre-strain and \( 1 \times 10^{-7} \) m for the specimen with 3\% pre-strain through \( L = 1/N^{1/2} \),

\[
\Delta \rho = \varepsilon / N^{1/2}
\]

respectively. Therefore, the lifetime of quenched-in excess vacancies \( \tau \) until annihilating at dislocations can be approximated at 298 K to be \( 4 \times 10^4 \)– \( 4 \times 10^5 \) s for the specimen without pre-strain and 7 s for the specimen with 3\% pre-strain through the following equation:

\[
\tau = L^2 / D_v
\]

where the diffusion coefficient for vacancies \( D_v \) is given by that for self-diffusion of aluminum \( D(T) \) and thermal equilibrium vacancy concentration \( C_v(T) \) at a temperature \( T \):

\[
D_v = D(T)/C_v(T).
\]

Here, \( D(T) \) is calculated with reported values of pre-exponential factor \( D_0 = 1.37 \times 10^{-5} m^2 s^{-1} \), activation energy \( Q = 123 kJ mol^{-1} \) for self diffusion and gas constant \( R = 8.31 J mol^{-1} K^{-1} \),

\[
D(T) = D_0 \exp(-Q/RT),
\]

whereas, \( C_v(T) \) is given as:

\[
C_v(T) = \exp(2.4) \exp(-73.3[kJ mol^{-1}]/RT).
\]

Although vacancies are annihilated even at other defects, e.g. grain boundaries, the above estimation of \( \tau \) indicates that dislocations induced by pre-straining effectively decreases the number of quenched-in excess vacancies, resulting in the sluggish diffusion of solute atoms. Therefore, it is concluded that pre-straining suppresses the formation of cluster(1) during single aging with more supersaturated solute atoms in the matrix. Since the earlier stages of phase decomposition are mainly investigated in this work, the different response of cluster(1) formation could be interpreted in term of kinetics of vacancy diffusion rather than the possible effect of vacancies for the nucleation of cluster(1).

### 4.2 Accelerated formation of the \( \beta'' \) phase by pre-straining

Figure 9 compares the hardness of the specimens without pre-strain and with 3\% pre-strain at each stage of heat treatments: i.e. before pre-aging \( HV(BP) \), after pre-aging at 298–373 K for 7.2 or 778 ks and after final aging at 443 K for 2.4 ks. The hardness changes during pre-aging and final aging can be obtained from the difference in hardness as shown by \( \Delta HV(FA) \) and \( \Delta HV(FA) \). From the results of the specimens pre-aged for 7.2 and 778 ks, it was found irrespective of pre-straining that \( \Delta HV(FA) \) increases with increasing pre-aging temperature, but decreases with increasing pre-aging time. The effect of pre-straining on bake-hardening response, \( \Delta HV(FA) \), strongly depends on the combined pre-aging conditions and is most effective if in combination with pre-aging at 343 K for a shorter time of 7.2 ks. The improved bake-hardening response by pre-straining is also shown by the shifts of exothermic Peak 2, attributed to the formation of the \( \beta'' \) phase, to lower temperatures in DSC traces (Fig. 4). Therefore, the combination of pre-straining and pre-aging is sufficiently applicable as a new process for improving strength of automotive body panels without diminishing the formability.

The accelerated formation of the \( \beta'' \) phase by the combined effect of pre-straining and pre-aging can be also explained from the difference in the amount of cluster(1), as is the case of the suppressed hardening in single aging (see section 4.1). Figure 10 shows the relationship between hardness change during final aging \( \Delta HV(FA) \) in Fig. 9 and heat of reaction for Peak 1 \( \Delta H_{P_eak1} \) in Fig. 8 for the specimens without pre-strain and with 3\% pre-strain, subjected to pre-aging in various conditions. It is clearly shown that \( \Delta HV(FA) \) increases with decreasing \( \Delta H_{P_eak1} \), irrespective of pre-aging conditions. This suggests that bake-hardening response at 443 K is mainly determined by the amount of cluster(1) formed during pre-aging. Therefore, the suppressed formation of cluster(1) by pre-straining is attributed to the increased bake-hardening response at 443 K due to the accelerated precipitation of the \( \beta'' \) phase from more supersaturated solute atoms.
5. Conclusion

The effect of pre-straining in combination with pre-aging on bake-hardening behavior of an Al-0.6 mass%Mg-1.0 mass%Si alloy was investigated by hardness test, electrical conductivity measurement, differential scanning calorimetry and transmission electron microscopy. It was found that pre-straining by 3% prior to pre-aging decreases the amount of pre-strain during single aging below 343 K, becomes less with increasing the amount of pre-strain. On the other hand, pre-straining improves bake-hardening response during final aging at 443 K up to 7.2 ks due to accelerated precipitation of the β' phase, as confirmed by TEM observation and DSC analysis. The effect of pre-straining on bake-hardening response strongly depends on the combined pre-aging conditions, and pre-straining by 3% is most effective if in combination with pre-aging at 343 K for 7.2 ks. This can be explained by suppressed clustering of solute atoms during pre-aging and accelerated precipitation of the β' phase from more supersaturated solute atoms during final aging, both of which are attributed to rapid annihilation of quenched-in excess vacancies at dislocations induced by pre-straining.

REFERENCES