Effect of Reversion on the Bake Hardening Response of Al-Mg-Si(-Cu) Alloy

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Abstract

The effect of reversion treatment on the bake hardening (BH) properties of Al-Mg-Si alloys has been investigated. When naturally aged Al-Mg-Si(-Cu) alloys are reversion heat-treated, bake-hardening response is improved. The GP zones that are formed during natural aging are completely dissolved by the reversion heat treatment, and coarser GP zones and β" precipitates are formed by the subsequent BH treatment. The change in the BH behavior as well as the effect of Cu addition are discussed based on the detailed microstructural characterization results by transmission electron microscopy (TEM), positron annihilation lifetime (PAL) measurement, coincidence oppler broadening measurement (CDB) and three dimensional atom probe (3DAP) analysis.

1. Introduction

Due to its excellent formability and medium strength after an age hardening, Al-Mg-Si based 6000 series alloys are considered to be the best candidate for automotive body sheet materials. In addition to the excellent formability and corrosion resistance, the alloy must exhibit age hardening during an automotive paint bake cycle, i.e. aging treatment at 170 – 175°C for approximately 20 – 30 min.

One serious problem of the Al-Mg-Si based alloy is its negative age hardening response after natural aging [1,2]. Although as-quenched solution treated sample shows substantial paint bake response, it does not show any bake hardening (BH) after natural aging. This two step aging process has been a subject of many investigations in 1960s and the research interest was recently revived due to its practical importance for automotive applications. Many investigations have been recently performed to improve the BH response such as optimization of alloy composition [3,4], addition of Cu [1,5-7], oppler g [8, 9] and reversion heat treatment [10]. Among these, this study focuses on the mechanism of the enhancement of the BH response by reversion after natural aging. In addition, we attempt to understand the effect of Cu addition in enhancing the aging kinetics as well as BH response. For this purpose, we have characterized the microstructures of commercial Si-excess Al-Mg-Si alloys with and without Cu by transmission electron microscopy (TEM), positron annihilation lifetime (PAL) measurement, coincidence oppler broadening measurements (CDB) and three dimensional atom probe (3DAP).

2. Experimental

Table.1: Chemical Composition.

Sample	unit	Mg	Si	Cu	Fe	Mn	Cr	Al
Ternary alloy	wt.%	0.6	1.0	-	0.15	0.08	-	Bal.
	at.%	0.67	0.96	-	0.07	0.04	-	Bal.
Cu-containing alloy	wt.%	0.5	1.05	0.7	0.15	0.08	0.08	Bal.
	at.%	0.56	1.01	0.29	0.07	0.04	0.04	Bal.

The chemical compositions of two alloys used in this study are shown in Table.1. Both alloys contain excess amount of Si with respect to the stoichiometry of Mg_2Si. One sample contains 0.3 at% Cu (Cu-containing alloy), and the other does not contain Cu (ternary alloy). The ternary and Cu-containing alloys were cut into square rods and 3 mm disks. The ternary and Cu-containing samples were solution treated at 550°C and 535°C, respectively, water quenched and then preaged at 70°C for 2 h following the industrial process. The samples were then stored at a room temperature for longer than three months (natural aging). For reversion treatment, the samples were soaked into an oil bath of 250°C for 30 s. These samples were aged at 170°C for 20 min (BH treatment), simulating the paint bake cycle in an automotive manufacturing process. For comparison, some samples were BH treated from the as-quenched state and after natural aging without reversion.

CDB method was employed to identify the solute-vacancy interaction by measuring the momentum distribution of the core electrons around the vacancies where positrons are trapped. The overall energy resolution is about 1.1 keV in full width at half-maximum (FWHM). A total count of more than 2×10^7 for each measurement was accumulated for 12h. Positron annihilation lifetime (PAL) was measured simultaneously with CDB measurement using a conventional fast-fast spectrometer with a time resolution of 190 ps in FWHM. The source of ^{22}NaCl deposited on a thin Kapton foil was sandwiched between two identical alloy specimens. The lifetime spectra were measured at 150K, and the total counts were 4×10^6 for each measurement of 12 h duration. TEM specimens were prepared by the conventional twin jet method. TEM observations were performed using a Philips CM200 TEM operated at 200 kV. The tomographic atom probe (TAP) and the energy compensated TAP (ECTAP) were employed for the characterization of elemental distributions. The samples were cut to 1×1×10 mm rods by a spark cutter and needle shaped specimens were prepared using the standard electropolishing technique. Atom-probe analyses were performed at a specimen temperature of ~20-30K in a ultrahigh vacuum (10^{-11} Torr) using a pulse fraction of 15 %.
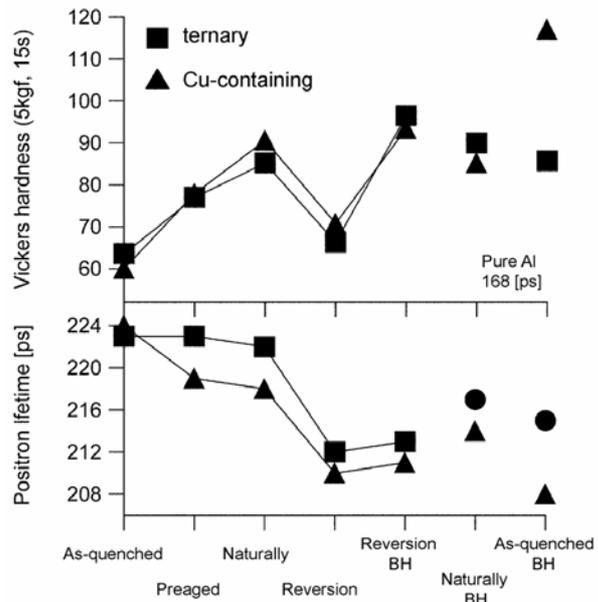

Figure 1: Vickers hardness and positron lifetime with various heat treatment conditions. The positron lifetime of well annealed pure Al exhibits 168 [ps].

3. Results and Discussion

Figure 1 shows Vickers hardness and PAL measurements results for various heat treatment conditions. Both alloys show increase in hardness after natural aging with a slightly higher hardness in the Cu-containing alloy. The hardness decreases by $\Delta H_v{\sim}20$ for both alloys after the reversion treatment, and the hardness level of the ternary alloy is nearly the same as that of the as-quenched sample. The hardness of the reverted Cu-containing alloy is higher than that of the as-quenched alloy by $\Delta H_v{\sim}10$. BH treatment right after the reversion treatment brought an increase in hardness of nearly $\Delta Hv{\sim}6$. However, the BH treatment applied to the naturally aged sample does not bring high BH response, namely, $\Delta H_v{\sim}13$ for the ternary alloy, and $\Delta H_v{\sim}7$ for the Cu-containing alloy. For comparison, the hardness of the samples that were BH treated immediately after a solution treatment were also measured (AsQ/BH). The Cu-containing alloy shows substantial hardening ($\Delta H_v{\sim}56$), but the ternary alloy shows much lower BH response ($\Delta H_v{\sim}21$).

Positron annihilation lifetime of each stage is also shown in Figure1. Although the solution treatment temperature for the ternary alloy was higher by 15°C than that for the Cu-containing alloy, the positron lifetimes of both the samples are almost the same (224ps). This lifetime is much longer than that for the well-annealed pure aluminum, 168ps [11], suggesting that a large number of quenched–in vacancies of the order of 10^{-5} in atomic fraction survive. It is interesting to note that the positron lifetime becomes shorter in the Cu-containing alloy than in the ternary alloy on aging. After preaging and natural aging, the positron lifetime of the ternary alloy does not change much, but those for the Cu containing alloy decreased from 224 to 217 ps. This suggests that a part of quenched-in vacancies annihilate in sinks in the Cu-containing alloy during preaging and the subsequent natural aging. On the other hand, in the ternary alloy, vacancies appear to be trapped with some solute atoms, hindering annihilation at vacancy sinks. After reversion, the positron life time decreased to 210ps in the Cu-containing alloy, 212ps in the ternary alloy. BH treatment of both reverted and naturally aged samples increase the lifetime slightly, suggesting that positron trap sites were created by the precipitation of the metastable phase that forms by the BH treatment. However, the lifetime of the Cu-containing sample that was BH treated immediately after quenching decrease to 208 ps. The decrease in the lifetime of the ternary alloy is more moderate, from 224ps to 216ps.
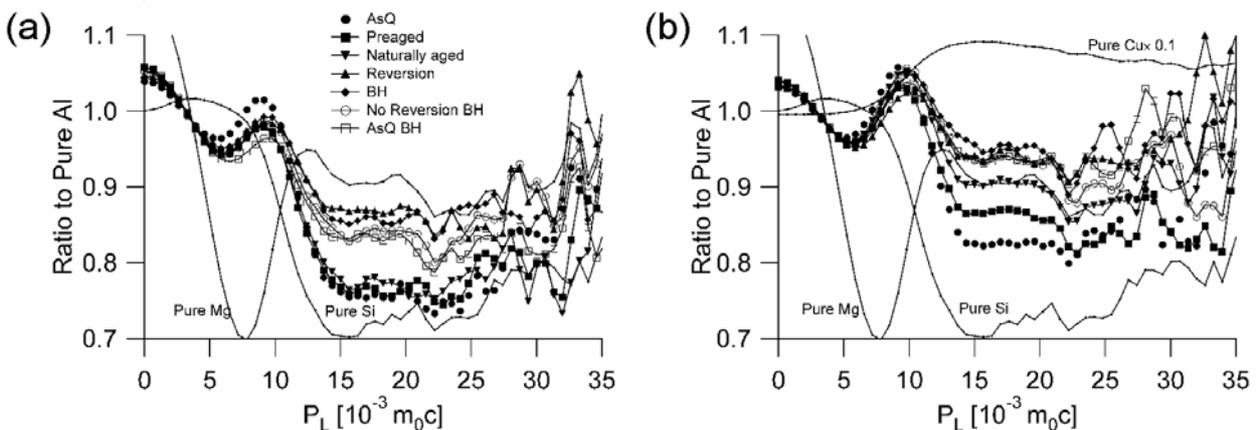
3.2 CDB Spectrum

Figure 2: CDB ratio curves for various heat treatment conditions (a) ternary and (b) Cu-containing alloys. Signals for Pure Mg, Pure Si and Pure Cu are superimposed experimental results.

Figure 2 shows CDB spectra with various heat treatments. The CDB spectra obtained from both ternary and Cu-containing alloys are similar and their changes after the heat

treatments are not so significant. This is because Mg and Si atoms are not sensitive to the CDB method because of their similar electronic shell structures to Al, which are in contrast to the case of Cu. However, the absence of the characteristic curve for Cu in the Cu-containing alloy indicates that vacancies are not bound to Cu atoms. This suggests that the rapid recovery of vacancies in the Cu-containing alloy shown in Figure 1 is not due to the Cu-vacancy interaction. So the kinetics enhancement due to the Cu addition is not because of the formation of Cu-vacancy complex.

3.3 Room Temperature Aging

TEM images of naturally aged samples are shown in Figure 3. Note that both samples were subject to preaging at 70°C for 2 h. Tiny spherical clusters or Guinier Preston (GP) zones are observed. These microstructures are very similar to that of previously observed images [12,13]. The GP zones in the Cu-containing alloy are much smaller in size with a larger number density than those in the ternary alloy, which would be the reason for the slight difference in hardness after natural aging.
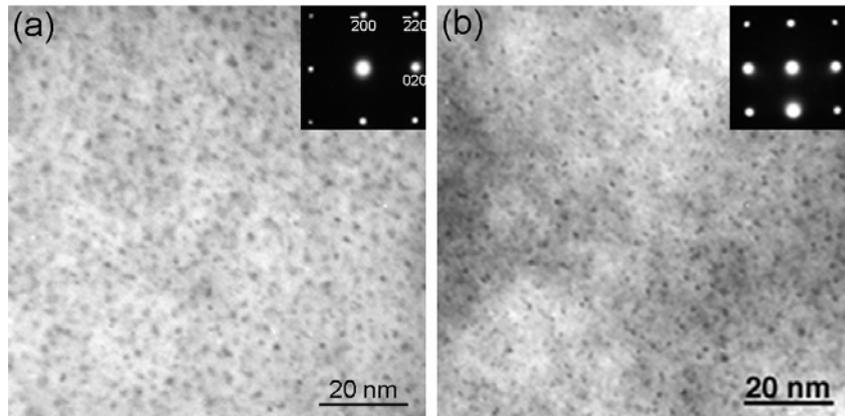

Figure 3: Bright field images and corresponding [001] SAED patterns of naturally aged (a) ternary and (b) Cu-containing alloys.

3.4 Bake Hardening Behavior

Figure 4 shows the H_v change of as-quenched, naturally aged and reverted samples plotted as functions of isothermal aging time at 170˚C. The vertical dotted line shows the BH condition (20 min at 170˚C). Industrial requirement is to obtain the highest hardness (strength) in the BH condition from the lowest initial hardness. The age hardening response within 20 min of aging is the highest in the as-quenched Cu-containing alloy. On the other hand, as-quenched ternary alloy shows rather slow age-hardening response in the initial stage. This clearly demonstrates that Cu enhances initial age hardening response. Naturally aged samples both show softening in the initial stage, and no bake hardening response is obtained in the BH condition. The
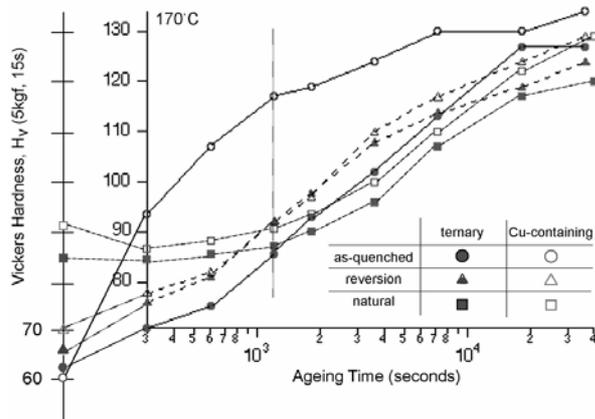

Figure 4: Isothermal age hardening curves for as-quenched, reversion treated and naturally aged samples, which were aged at 170˚C.

Cu-containing sample shows more adverse effect. On the other hand, the reverted samples show improved BH response ($\Delta H_v\sim26$ for the ternary alloy and $\Delta H_v\sim21$ for the Cu-containing alloy).
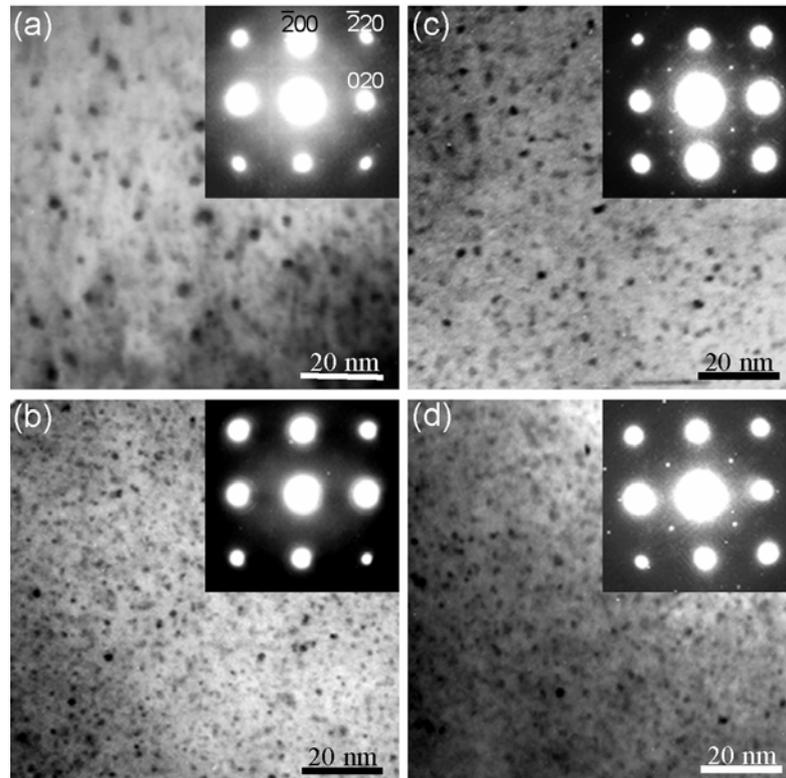

Figure 5: Bright field images and corresponding [001] SAED patterns of ternary alloy (a) reversion treated, (b) naturally aged followed by BH, and of Cu containing alloy (c) reversion treated and (d) naturally aged followed by BH.

Figure 5 shows TEM bright field images of the sample that was BH treated after reversion and the one that was BH treated without reversion after natural aging. The precipitate particles observed in the BH treated samples after reversion are larger than those in the BH treated samples after natural aging. The SAED pattern in Figure 5 (a) indicates that β" precipitates are present. Since TEM image show spherical particles, we conclude that both GP zones and β" precipitates coexist in this specimen

The Cu-containing alloy that was BH treated after reversion shows much finer microstructure than the ternary alloy with the same heat treatment. The SAED pattern shows that the precipitates are β", although bright field image does not show clear rod-like feature of β" precipitates. Thus we can conclude that the precipitates in the reversion/BH treated Cu-containing alloy are mostly β". The BH treated ternary alloy without reversion show fine spherical particles. No diffraction evidence for the presence of β" precipitates is seen, hence we conclude that the sample contains only GP zones. On the other hand, the SAED pattern of Cu-containing alloy shows the presence of β" precipitates in addition to the GP zones. Streaks are observed along the <100> matrix directions in Figure.5 (a), (c), and (d), which have been attributed to the β" phase [1,12,13,14-17].
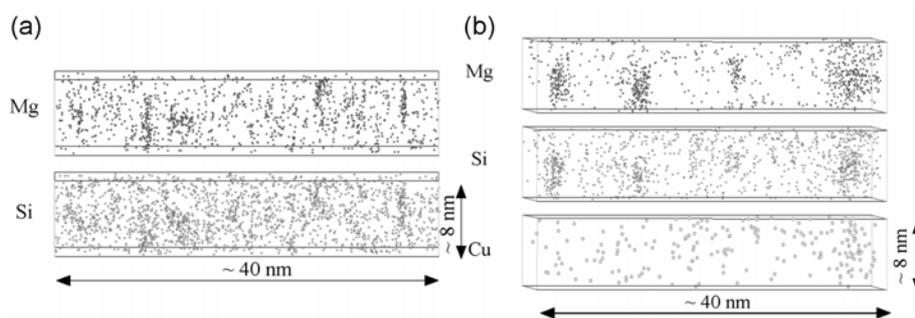
Figure 6: Elemental mapping of Mg, Si and Cu in (a) ternary and (b) Cu-containing alloys, aged at 170˚C for 20min (BH treated) after reversion treatment.

Figure 6 shows 3DAP map of Mg, Si, and Cu atoms obtained from (a) ternary and (b) Cu-containing alloys that were BH treated after reversion. The box size is approximately ~ 8×8×40 nm, and a probe direction is parallel to the matrix [022] direction. The TEM images for these samples are shown in Figure 5 (a) and (b), respectively. The size of the spherical particles observed in Figure 6 (a) is approximately 4 nm, which is consistent with the BF image in Figure 5 (a). In addition to the spherical particles, precipitates elongated to the [001] direction are also seen in this map, which are believed to be needle like β“ phase. On the other hand, only elongated β“ precipitates are observed in the Cu-containing alloy parallel to the [001] matrix direction. Note that Cu is partitioned into β“ phase in this stage, in agreement with the previous atom probe results [12].

4. Summary

Transmission electron microscopy, three dimensional atom probe and positron annihilation techniques were employed to study the effect of reversion on the BH response of Si-excess Al-Mg-Si(-Cu) alloys. Although the vacancy concentrations were estimated to be nearly the same in the as-quenched state of both ternary and Cu-containing alloys based on the positron annihilation lifetimes, the vacancy concentrations are lower in all heat treated Cu-containing alloys. Rapid decrease of vacancies in the Cu-containing alloy during preaging and natural aging as well as BH treatment from the as-quenched state explains observed pronounced BH response from the as-quenched Cu-containing alloy. However, CDB results did not indicate that this rapid decrease of vacancies in the Cu-containing alloy was due to the formation of Cu-vacancy complex. Both alloys did not show any BH response after natural aging, but the hardness of the Cu-containing alloy after BH was slightly higher because of higher initial hardness after natural aging. Reverted samples showed pronounced BH response in both samples compared to the naturally aged ones. In the Cu-containing alloy, the precipitates formed after BH treatment were all β“, while GP zones and β“ precipitates coexist in the BH treated ternary alloy.

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